The Stable Isotopic and Anionic Composition of the Avon and Heathcote River Systems, Christchurch, New Zealand: a study of lowland spring-fed rivers in a seismically active environment

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A thesis submitted in partial fulfillment of the requirements for the degree of

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By

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Abstract

The Avon and Heathcote Rivers, located in the city of Christchurch, New Zealand, are lowland spring-fed rivers linked with the Christchurch Groundwater System. At present, the flow paths and recharge sources to the Christchurch Groundwater System are not fully understood. Study of both the Avon and Heathcote Rivers can provide greater insight into this system. In addition, during the period 2010-2012, Christchurch has experienced large amounts of seismic activity, including a devastating M_w 6.2 aftershock on February 22nd, 2011, which caused widespread damage and loss of life. Associated with these earthquakes was the release of large amounts of water through liquefaction and temporary springs throughout the city. This provided a unique opportunity to study groundwater surface water interactions following a large scale seismic event.

Presented herein is the first major geochemical study on the Avon and Heathcote Rivers and the hydrological impact of the February 22, 2011 Christchurch Earthquake. The Avon, Heathcote, and Waimakariri Rivers were sampled in quarterly periods starting in July 2011 and analyzed for stable Isotopes $\delta^{18}O$, δD, and $\delta^{13}C$ and major anion composition. In addition, post -earthquake samples were collected over the days immediately following the February 22, 2011 earthquake and analyzed for stable isotopes $\delta^{18}O$ and δD and major anion composition. A variety of analytical methods were used identify the source of the waters in the Avon-Heathcote System and evaluate the effectiveness of stable isotopes as geochemical tracers in the Christchurch Groundwater System.

The results of this thesis found that the waters from the Avon and Heathcote Rivers are geochemically the same, originating from groundwater, and exhibit a strong tidal influence within 5km of the Avon-Heathcote Estuary. The surface waters released following the February 22nd, 2011 earthquake were indistinguishable from quarterly samples taken from the Avon and Heathcote Rivers when comparing stable isotopic composition. The anion data suggests the waters released following the February 22nd, 2011 Christchurch Earthquake were sourced primarily from shallow groundwater, and also suggests a presence of urban sewage at some sites. Attempts to estimate recharge sources for the Avon-Heathcote Rivers using published models for the Christchurch Groundwater System yielded results that were not consistent between models. In evaluating the use of geochemical constituents as tracers in the Christchurch Groundwater System, no one isotope could provide a clear resolution, but when used in conjunction, $\delta^{18}O$, $\delta^{13}C$, and DIC, seem to be the most effective tracers. Sample sizes for $\delta^{13}C$ were too small for a robust evaluation. Variability on the Waimakariri River appears to be greater than previously

estimated, which could have significant impacts on geochemical models for the Christchurch Groundwater System. This research demonstrates the value of using multiple geochemical constituents to enrich our understanding of the groundwater surfaces-water interactions and the Christchurch Groundwater System as a whole.

Acknowledgements

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Chapter 1: Introduction

1.1 Background

The Avon and Heathcote Rivers are lowland spring fed rivers, and are major features of the City of Christchurch, New Zealand, providing both aesthetic and economic value. Groundwater is an incredibly important economic resource in New Zealand and for Christchurch in particular, as it relies solely on groundwater for its public water supply. The groundwater of the Christchurch Groundwater System is of extremely high quality. It can be utilized without treatment and is easily extracted from artesian aquifers directly beneath the city. While groundwater abstraction rates for the city are known, calculating the flow paths, sources and replenishment rates for the Christchurch Groundwater System have proven to be a considerable challenge (Talbot 1986, Taylor 1989, Brown and Weeber 1992, White 2009, Stewart 2012).

In the past two years Christchurch has experienced a large number of significant seismic events starting with a 7.1 Mw earthquake in September 2010. The most devastating event was a 6.3 Mw aftershock on February 22nd, 2011 which resulted in loss of life and significant damage to infrastructure. Causing an estimated US $10 billion or more worth of damages it is New Zealand's most expensive natural disaster since the 1931 Hawke's Bay earthquake (Quigley et al 2011). These earthquakes also had a significant hydrological impact on the city, by releasing large amounts of liquefaction and creating a number of temporary springs.

The Avon and Heathcote Rivers provide an opportunity to study surface-water, groundwater interactions in the Christchurch Groundwater System, adding to our understanding of this important system. The Avon and Heathcote Rivers also provide a unique opportunity to study the surface-water, urban-water, groundwater interactions. It is my theory that geochemistry, in particular stable isotope geochemistry, can provide a valuable tool when used in conjunction with other geochemical tracers, for determining the sources and origins of the waters feeding the Avon and Heathcote as well as the sources of waters released during the February 22nd earthquake.

1.2 Scope for Thesis

1.2.1 Thesis Objectives

The goal of this research is to see how the geochemical composition of the of Avon and Heathcote Rivers varies both spatially and temporally, and how the Rivers fit into the greater context of the Christchurch Groundwater System. The secondary goal of this research is to attempt and identify what, if any, changes occurred along the Avon River following the February 22nd, 2011 Christchurch earthquake and how the surface waters released following this earthquake relate to the Christchurch Groundwater System.

1.2.2 Thesis Organization

This thesis is organized into 7 main chapters and a bibliography.

Chapter One: Introduction

Chapter one introduces the background, object and organization of the thesis. From there it introduces groundwater and the need for hydrological research in Canterbury.

Chapter Two: Geochemical Tracers in Hydrology

Chapter two covers the use of geochemical tracers in hydrological studies. It starts with a review of hydrology, followed by an explanation of geochemical tracers, such as stable isotopes, in hydrology.

Chapter Three: Study Area and Geologic Setting

Chapter three introduces the study area and the local and regional geologic context. It presents an overview of the regional tectonic setting, bedrock geology and recent (2010-2012) seismic activity. From there it discusses the surficial geology of the study area followed by an overview of the hydrology of the Christchurch Groundwater System.

Chapter Four: Methodology

Chapter four covers the methods involved of gathering and processing water samples, from the selection of sites to analyses in the labs.

Chapter Five: Results

Chapter five presents the data collected during the course of this thesis. It is broken up into individual geochemical tracers and presents the range of samples collected, median and mean.

Chapter Six: Discussion

Chapter six discusses the data collected for this thesis, identifying trends in the Avon and Heathcote Rivers, examining the impact of the February 22nd, 2011 earthquake, comparing it the previous studies on the Canterbury Groundwater System and evaluating the effectiveness of geochemical tracers in these systems.

Chapter Seven: Conclusion

Chapter seven concludes this thesis, summarizing its key findings and proposing further avenues of research.

1.3 Water

1.3.1 Global Water Resources

Freshwater is a critical global resource as it is a necessity for living, growing crops and used in almost every industry. In short, modern living would be impossible without access to supplies of clean freshwater. The vast majority of water in the world, roughly 97%, is located in the oceans, and currently unusable without extensive and expensive treatment. The remaining 3% of water on earth is freshwater, split between, in order of largest to smallest reservoir, the Cryosphere, Groundwater, and Surface water.

The Crysophere comprises roughly 69% of the worlds freshwater. From a resource standpoint it is mostly inaccessible, locked away in the Antarctic and Greenland icecap. Mountain glaciers are indirectly important water sources, recharging rivers in mountainous regions such as the Himalayas. Groundwater is the second largest freshwater reservoir, comprising roughly 30% of the worlds freshwater (Fetter 2001). As a resource groundwater is relatively clean, reliable and cost effective, especially in areas with limited or polluted surface water resources, and in arid regions often constitutes the primary source of freshwater (Bovolo et al 2009). Surface water is the smallest freshwater reservoir at .3%, with the majority of surface water stored in lakes and ponds.

1.3.2 Water Resources in New Zealand

New Zealand has abundant water resources, due to high precipitation rates, runoff and relatively large storage volumes in the form of natural reservoirs, e.g. groundwater and snowpack. Groundwater is the largest storage reservoir for freshwater in New Zealand, storing an estimated 80%, $1.7 \times 10^{12} m^3$, of its freshwater (Toebes 1972, Brown 2001). While abundant, the distribution and volume of freshwater supplies varies with geology, climate, and hydrologic stresses, e.g. abstraction (White 2001).

Freshwater has been utilized for a number of different applications in New Zealand, such as, hydro-electric generation, irrigation and water supplies (Waugh 1992). Groundwater usage accounts for approximately 30% of New Zealand's freshwater usage, though the number is probably higher as this figure does not take into account individual domestic supplies and stock-water systems (White 2001). At approximately 74% of allocated groundwater, irrigation is the largest allocation, with community water supplies accounting for only 17% of the total allocation (White 2001). Despite being a relatively small portion of the total groundwater allocation, groundwater is a very important source of drinking water for cities in New Zealand. It is estimated that 26% of the New Zealand population relies on groundwater as their sole source of drinking water, and another 25% of the population drink water sourced from both groundwater and surface water (White 2001). A number of cities are totally dependent on groundwater for their public water supply, these include, Wanganui, Napier, Hastings, Lower Hutt, and Christchurch.

1.3.3 Water use in Christchurch and Canterbury

Currently the Canterbury Region is the largest user of groundwater in New Zealand (Lincoln Environmental 2000). Approximately 85% of this use is for irrigation, and in many areas of Canterbury allocation rates exceed annual recharge rates for recharge zones. Groundwater is used in urban areas of Canterbury; most notably groundwater is the sole source of public reticulated water for the City of Christchurch. The CGS, is sourced from a series of artesian aquifers underlying city, and is able to be easily extracted and used without treatment. Groundwater is also the source of water for many streams along coastal Canterbury such as the Avon and Heathcote rivers in Christchurch. Average annual abstractions from the CGS are ~ 104 x 10^6 m^3/year(Talbot 2010). Calculating the flow paths, sources and annual replenishment rates for the CGS has been a difficult challenge, requiring further research and long term monitoring (Talbot 1986, Taylor 1989, Brown 2001, Stewart 2012)

Chapter 2: Geochemical Tracers in Hydrology

2.1 Introduction

This chapter introduces the geochemical tracers used to track water movements through reservoirs in the hydrologic cycle. First, this chapter presents an overview of how water moves through earth's systems in a process known as the hydrological cycle. Second, a brief summary of psychical hydrology and surface-groundwater interaction is presented. Third, the chapter provides an overview of the principles of stable isotope geochemistry and its application to hydrological problems is presented. Fourth, the chapter concludes with an examination of the use of dissolved solutes as tracers in catchment scale hydrology.

2.2 Hydrology: a review

2.2.1 The Hydrologic Cycle

The hydrological cycle is a generalized conceptual model of how water moves through the earth system. Mass fluxes in the hydrological cycle include evaporation, transpiration, precipitation, surface runoff and infiltration (Figure 2.1). As the largest water reservoir, oceans are generally considered the start and end of the hydrologic cycle as well as the source from which all water is ultimately derived. Water evaporates from the oceans into the atmosphere. Evaporation rates vary around the world, with the highest rates near the equator, as equatorial regions receive the greatest amount of solar radiation. In the atmosphere water vapors then transported around the globe and depending on atmospheric conditions precipitated onto land masses or back into the oceans. More localized hydrologic cycles can occur over land as water is evaporated into the atmosphere from lakes and rivers or from plants via transpiration and precipitated once more. In the terrestrial environment water enters temporary storage, being held in glaciers, groundwater, lakes or rivers. All water eventually cycles back into the ocean though residence times can vary greatly between reservoirs. The average residence time water is the atmosphere is in approximately 9 days, while residence times for rivers can vary between days to years. Groundwater is the second largest terrestrial reservoir with some of the longest residence times, which range in the order of decadal to centennial scales. The hydrologic cycle is however, a simplification of an incredibly complex system that is functioning on a global scale. On the local and

regional scale, hydrological processes are more complicated than this model and require more sophisticated approaches in order to understand movements between reservoirs.

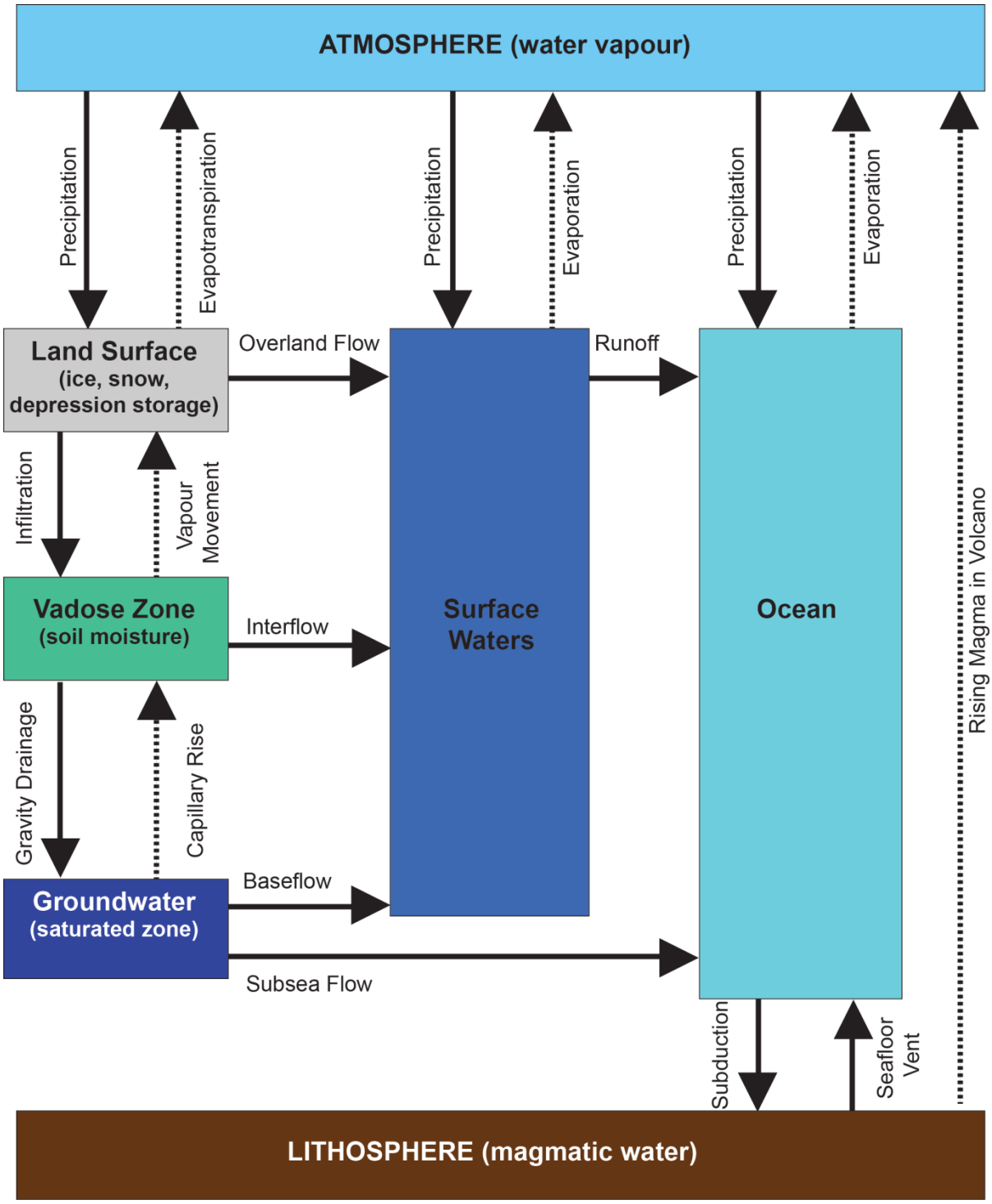

Figure 2.1 A conceptual model of the hydrologic cycle. Boxes represent the hydrologic reservoirs and arrows indicate fluxes between reservoirs (modified by Blackstock 2011 from Fetter 2001).

2.2.2 Catchment Hydrology

Hydrology at any scale can be described with a simple mass balance model, in effect restating the law of mass conservation (Equation 2.1). This model is known as the continuity equation and is expressed as:

$$\text{Inflow} = \text{Outflow} \pm \text{changes in storage}$$

Equation (2.1)

In this equation, all three parameters have units of volume per time. In surface hydrology the continuity equation is typically applied at catchment or sub-catchment scales. Catchments, or drainage basins, are areas of land were meteoric waters converge towards a single point usually the exit of the basin, e.g., a river flowing into a lake, ocean or a larger river. Catchments can be further broken into sub-catchments. For example a large river can have many sub catchments for each tributary which in turn can have its own sub-catchments (Figure 2.2).

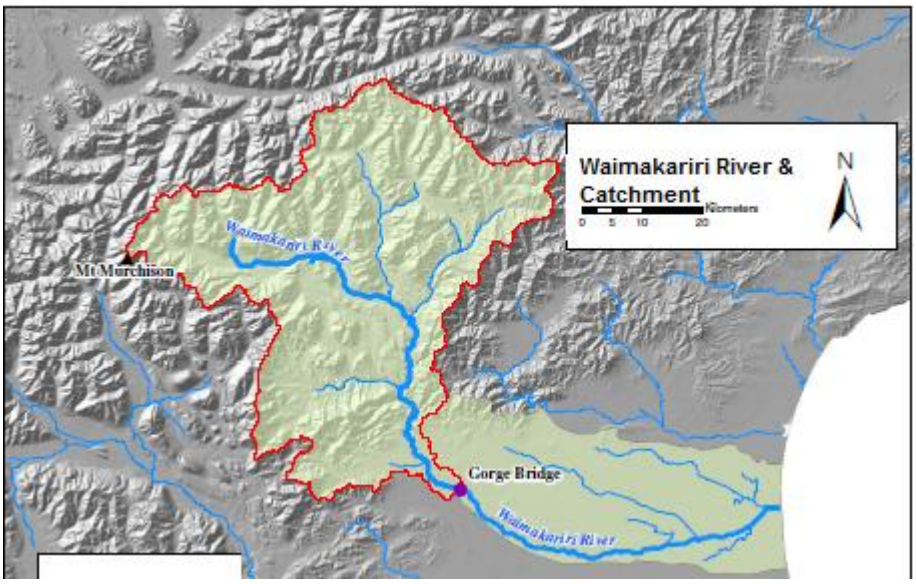

Figure 2.2 Catchment for the Upper Waimakariri River. This a sub-catchment for the Waimakariri River, and each branch can be further broken into sub-catchments . (Modified from Lu, X 2009).

2.2.3 Groundwater

The largest accessible hydrologic reservoir, groundwater is defined as water that exists below the water table; the area above the water table but below the land surface is the vadose zone. In the vadose zone pore spaces contain water, gases and air, at less than atmospheric pressure; it is also referred to as the unsaturated zone (Fetter 2001). Groundwater flows through the pore space between grains in sediments, or through fractures in bedrock. A measure of the amount of pore space in a material is

referred to as porosity, and generally sediments with larger grain size have greater porosity. Pore space is intrinsically linked to permeability which is a measurement of the ability of a porous material to allow fluids to flow through it. This is why course grained sediments, such as gravels, which have large pore spaces, have high permeability. High porosity, however, is not always associated with high permeability. Clays for instance have high porosity but very low permeability, because pore space in clays can hold a large volume of water, due to the structural of clays, but the pore space is not connected allowing water to readily flow through the material.

Modern groundwater hydrology started in 1856 when Henry Darcy working in Dijon, France made the first systematic attempt to understand how water flows through a porous media. Darcy's experiments studied the movement of water through a pipe packed with sands, and showed that discharge is proportional to the difference in height of the water (hydraulic head) and is inversely proportional to the flow length. This discovery, taking into account the cross-sectional area of the pipe, can be expressed in a mathematical equation known as Darcy's law (Equation 2.2)

$$Q = -KA\frac{\Delta h}{\Delta l}$$

Equation (2.2)

Where, Q, is discharge, with units of volume per time, K is the hydraulic conductivity, a measure of permeability measured in length per time, A is the cross-sectional area and Δh/Δl is the hydraulic gradient, or the change in hydraulic head, a unitless parameter.

Groundwater reservoirs which allow the flow of water are called aquifers. Aquifers are geologic units that can store and transmit waters, which due to varying lithologies and host sediment properties, can have greatly differing storage and transmission properties. Principally there are three types of aquifers, unconfined, confined, and leaky (Figure 2.3). Unconfined aquifers, also called open aquifers, are aquifers overlain by continuous layers of permeable material allowing for the unrestricted flow of groundwaters. Confined aquifers are overlain by confining layers which have relatively little permeability, restricting groundwater flow within the aquifer. Leaky aquifers, also known as semi-confined aquifers, are partially confined aquifers where the confining layer is either non-continuous or allows some flow of water across the confining layer. Recharge to confined aquifers can occur in multiple ways; in some cases the confining layer may allow very slow infiltration and recharge, while in other cases the aquifer may have a recharge zone where either the aquifer crops out to the land surface or the confining layer is absent.

Artesian aquifers are a special type of confined aquifers, where water in the confined aquifer is under pressure. Wells sunk into these aquifers will rise above the top of the aquifer, and in some cases may rise above the land surface forming a flowing artesian well.

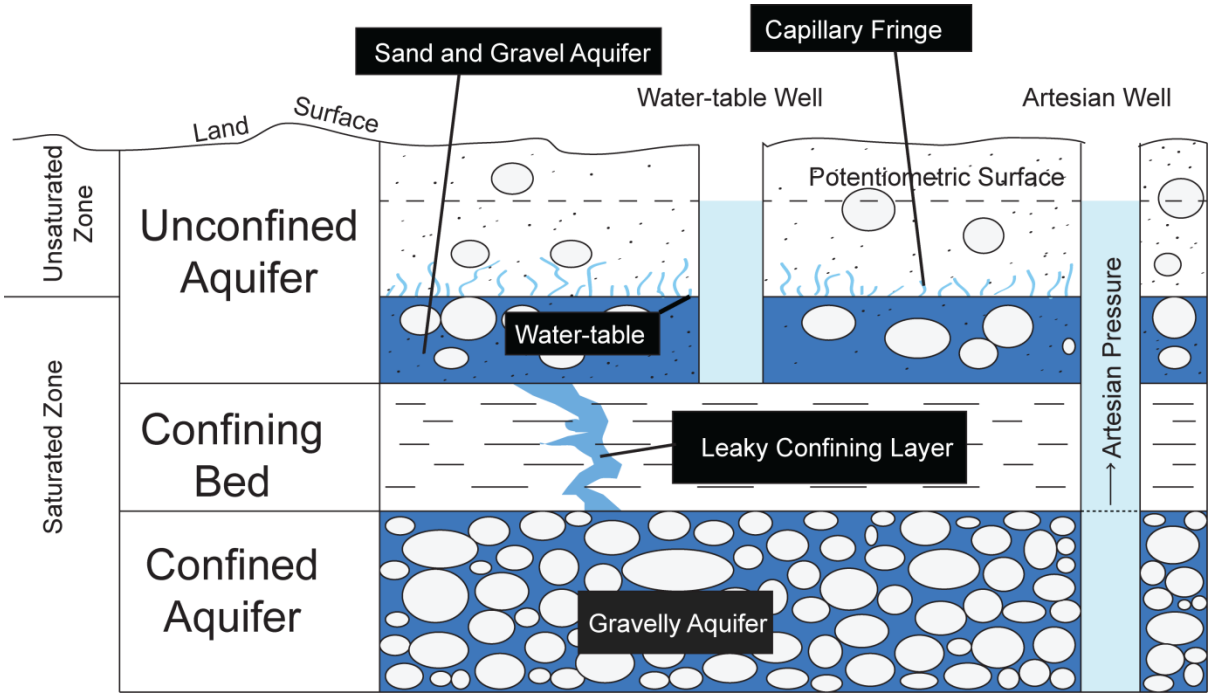

Figure 2.3 The three types aquifers: Unconfined, confined and leaky. When groundwater in a confined aquifer is under pressure wells tapped into the pressurized groundwater can rise above the normal water table in what is referred to as artesian pressure (modified from Heath 1983) and used with permission from Blackstock 2011.

Mapping of flow direction in wells is made by mapping the potentiometric surface, the water level of wells within a single aquifer. The potentiometric maps are essentially topographic maps for water, with the contour lines representing hydraulic head, water table, for an area. Surface waters, such as lake, streams and rivers can interact with the water table, and will be discussed in the next subsection (Figure 2.4). The water table usually reflects the surface topology of the area, as groundwater will flow from areas with high water tables to areas with low water tables, or put another way water will always flow from areas of high pressure to areas of low pressure.

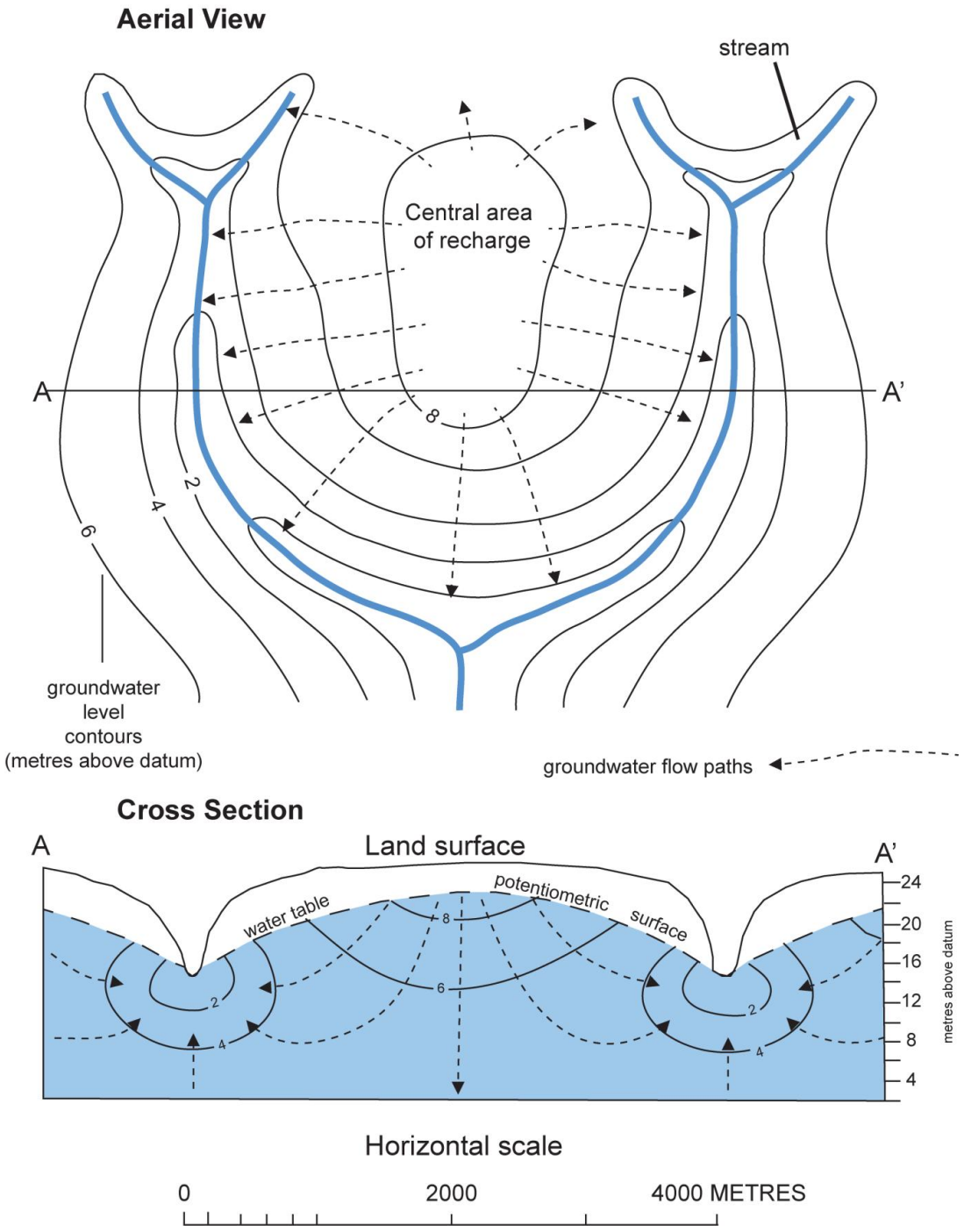

Figure 0.4: **A potentiometric map. Water will always flow from areas of higher hydraulic head to areas with lower head. Groundwater flows perpendicular to contours on a potentiometric map. modified from Heath 1983 (Used with Permission from Blackstock 2011).**

Surface hydrology and groundwater hydrology are intertwined, and when studying surface systems it is crucial to understand the local groundwater hydrology. Surface waters can be recharged by or act as sources to groundwater. Spring-fed rivers for instance, such as the Avon and Heathcote Rivers of Christchurch, are directly sourced by groundwater and any study on these systems would be incomplete without a understanding of groundwater-surface water interactions.

2.2.4 Recharge and groundwater-surface water interactions

Surface water recharge can occur in a number of ways and is intrinsically linked to groundwater. Water falling during precipitation events can recharge both groundwater and surface water. Direct precipitation onto streams is insignificant in most cases, but can be significant for lakes (Fetter 2001). During precipitation events water can infiltrate into permeable, unsaturated, soil which, when a portion of it reaches the water table, recharges groundwater. If soil permeability is not uniform, interflow or horizontal flow through soil can occur. Soil has a limited infiltration capacity, based on a number of factors including soil type and the amount of soil moisture, and, when infiltration capacity is reached or exceeded precipitation will remain on land surface. Precipitation can be stored in depression storage, e.g. puddles, or flow overland in a process called Horton overland flow (Fetter 2001). Overland flow only occurs when precipitation rates exceed inflation capacity rather than match it. Overland flow, however, is rarely observed outside of urban and suburban areas were human infrastructure has drastically increase the amount of impermeable land. Overland and interflow can contribute substantially to runoff in some catchments (Fetter 2001).

Rivers can recharge or be recharged by groundwater, or, do both depending on reach-scale conditions (Figure 2.5). Rivers recharged by groundwater are referred to as gaining streams, while rivers which recharge water, essentially losing water to groundwater, are called losing streams. A stream which is normally a gaining stream during baseflow conditions can become a losing stream during periods of heavy precipitation or flooding, when its water table raises above the groundwater's water table. During these times the raised water table near the banks of the river is referred to as bank storage and the water table will return to normal as baseflow conditions are met.

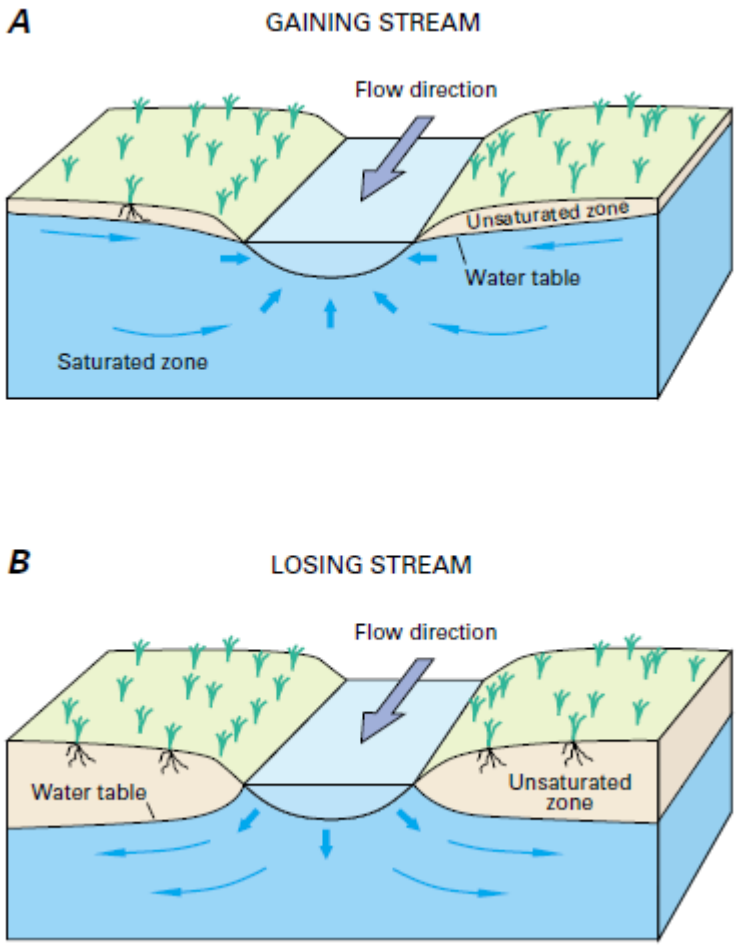

Figure 2.5 Gaining Streams (A) and Losing Streams (B) (modified from Alley et al 1999)

2.3 Stable Isotope Geochemistry

2.3.1 Historical Background

While there were suggestions that isotopic fractionation of light elements could occur in natural substances in the 1920s, it was with the discovery of the stable isotope, deuterium in 1931 by H. Urey and colleagues at Columbia University, which marked the beginning of stable isotope geochemistry, and won Urey a Nobel Prize in chemistry in 1934. The major progress in the stable isotope field over the next 30 years was carried out physicists and chemists and focused on refining precision of isotopic measurements and analytical methods. It quickly became apparent that stable isotopes were potentially

powerful tools with many applications in the geosciences, including determining temperature of rock formation, paleotemperature reconstruction, and had applications in the field of hydrology.

While there was earlier work involving stable isotopes and the hydrosphere, it was with two landmark papers in 1953 by one by Friedman, and the other Epstien and Mayeda which the development of the field of stable isotope hydrology began in earnest (Table 2.1). These papers began to establish the relationships between the physical chemical processes of fractionation and observed natural isotopic concentrations in the atmosphere, hydrosphere and biosphere. Through the 1960s considerable work was done on a global scale, most notably by Dansgaard and Craig, which established on a quantitative basis the relations governing variations in meteoric waters.

Year	Title	Reference
1932	A hydrogen isotope of mass 2 and its concentrations	(Urey et al. 1932)
1935	Isotopic exchange equilibria	(Urey & Greiff 1935)
1935	The relative atomic weight of oxygen in water and air	(Dole, 1935)
1950	Isotopic composition of oxygen in silicate rocks	(Baertschi, 1950)
1952	Variation in the relative abundance of carbon isotopes in plants	(Wickman, 1952)
1950	Improvements in Mass Spectrometers for the Measurement of Small Differences in Isotope Abundance Ratios.	(McKinney et al., 1950)
1953	Variation of ^{18}O content of waters from natural sources	(Epstein and Mayeda, 1953)
1953	Deuterium content of natural water and other substances	(Friedman 1953)
1961	Isotopic variations in meteoric waters	(Craig 1961)
1964	Stable isotopes in precipitation	(Dansgaard 1964)

Table 2.1 Selected important publications in Stable Isotope Geochemistry. Modified from Sharp 2007

2.3.2 What are Isotopes?

The atom is a basic unit of matter and is composed of a central nucleus of positively charged protons and neutral neutrons around which orbits a cloud of negatively charged electrons. An element and its properties are determined by the number of protons in an atom, referred to as the atomic number. In isotope geochemistry, chemical notations are carried out using an elements mass number, the total number of protons and neutrons in the element. For instance oxygen's atomic number is 8, while its mass number is usually 16, indicating 8 protons and 8 neutrons are present in the nucleus and is noted as ^{16}O. An isotope of a given element will share the same number of protons but will have a different number of neutrons. For example, there are three stable isotopes of oxygen, ^{16}O, ^{17}O, and ^{18}O; each has 8 protons but a varying number of neutrons, 8, 9, and 10 respectively.

Isotopes can fall into three categories, stable, radiogenic and radioactive isotopes. Radioactive isotopes, such as ^{14}C, are unstable and undergo radioactive decay under set decay rates. Radiogenic isotopes are the product of radioactive decay.^{14}N is an example of a radiogenic isotope and is formed by the decay of the radioactive isotope ^{14}C. Knowing the decay rate and measuring the relative amounts of parent to daughter products forms the basics of radiometric dating. In hydrological studies the radioactive isotope of hydrogen, tritium, ^{3}H, with a half-life of 12.3 years, is often used to date and track movement of relatively young waters. Stable Isotopes on the other hand do not undergo radioactive decay; in theory stable isotopes could undergo spontaneous decay but the probability of this happening is negligible (Sharp 2007).

2.3.3 Stable Isotope Ratios and Standards

Because it's incredibly difficult to accurately measure absolute isotopic compositions, measurements in stable isotope geochemistry are given as ratios. These ratios can be determined with great accuracy and are given in delta notation, introduced in 1950 by McKinney. Delta notation is the ratio of abundance of heavy isotopes to light isotopes. Delta notation is given in units of per mil, ‰, or parts per thousand, relative to a particular reference standard (Equation 2.2) (McKinney et al 1950, Sharp 2007).

$$\delta = \left(\frac{R_{sample} - R_{standard}}{R_{standard}}\right) \times 1000\ ‰$$

(Equation 2.2)

When presenting stable isotopic data in delta notation, using oxygen isotopes as an example, the data would be reported as $\delta^{18}O$, rather than writing out $^{18}O/^{16}O$.

In order to compare isotopic data from various labs around the world a set of international reference standards have been made. Though it is beyond the scope of this chapter to explain the history of how these reference standards were chosen, Sharp (2007) provides an excellent overview for curious readers. For isotopes of hydrogen and oxygen, often used in hydrologic studies, the reference standard currently in use is SMOW, also known as V-SMOW, for Vienna Standard Mean Ocean Water. This standard was established as an approximate average of oceanic water as the ocean is the largest reservoir of water in the hydrologic cycle. This standard, established in a series of conferences in Vienna, puts the value for oxygen and hydrogen, $\delta^{18}O$ and δD, respectively as 0.0 ‰. Individual labs generally use a working standard which has been calibrated to certified samples of SMOW.

Due to Rayleigh fractionation, which will be discussed later, most materials are negative in comparison to SMOW. Due to the nature of mass spectrometers deuterium readings of ±20-30‰ or more from the working standard will vary between mass spectrometers. Because deuterium has large variations in isotopic compositions in nature, it is necessary to correct readings using a two point calibration. Apart from SMOW, there is second reference standard in use called Standard Light Antarctic Precipitation., SLAP, which is based off of isotopically light, i.e. depleted in ^{18}O and D, waters from Antarctica.

2.3.4 Stable Isotopes and Isotopologues of Water

The use of stable isotopes in most hydrological studies focuses on the abundance of stable isotopes of hydrogen and oxygen, principally deuterium (D) and Oxygen-18(^{18}O). Hydrogen has two stable isotopes, protium and deuterium, while oxygen has three, oxygen -16, oxygen -17 and oxygen -18 (Table 2.2).

Stable Isotope	Average abudance (%)
H (protium)	99.9844
D (deuterium)	0.01557
^{16}O	99.7621
^{17}O	0.03790
^{18}O	0.20004

Table 2.2 Relative abundances of Hydrogen and Oxygen Stable Isotopes on Earth (modified from Sharp 2007)

Since each constitute element can contain a stable isotope, molecules, such as water, H_2O, can have different isotopic forms referred to as Isotopologues. Isotopologues are molecules that differ from one another only in isotopic composition. There are nine possible Isotopologues of water, with varying abundances, the most common of which unsurprisingly is $H_2{}^{16}O$ (Table 2.3) (Kendal and Coplen 2001, Sharp 2007). Due to the low abundance, and difficulty of detecting, isotopologues containing two or more uncommon stable isotopes per molecule most studies focus on $H_2{}^{18}O$ and $HD^{16}O$.

Isotopologue	Average abundance (%)
$H_2{}^{16}O$	99.73098
$H_2{}^{18}O$	0.199978
$H_2{}^{17}O$	0.031460
$HD^{16}O$	0.0000006
$HD^{18}O$	0.0000001
$D_2{}^{16}O$	0.00000002
$D_2{}^{17}O$	0.0000000001
$D_2{}^{18}O$	0.0000000005

Table 2.3 Relative abundances water Isotopologues (modified from Sharp 2007)

2.3.5 Controls on the Stable Isotopic Composition of the hydrosphere

Variations in the stable isotopic composition of precipitations, and ultimately across the hydrosphere, are a result of fractionation. Isotope exchange reactions can occur as either equilibrium or kinetic reactions. For example, condensation is an equilibrium process dependent on temperature, while evaporation is a kinetic process, with fractionation depending on a number of factors. In equilibrium fractionation the forward and backward reaction rates of any particular isotope are identical; however this does not mean that isotopic compositions of two components in equilibrium are identical (Kendall and Coplen, 1998). Because of mass differences the internal energies of different isotopes are slightly different causing a slight preference for heavier isotopes to be partitioned into one phase relative to another, such as liquid compared to vapor. For a thorough explanation of equilibrium fractionation, refer to or Sharp (2007).

In kinetic fractionation, the forward and backward reaction rates are not identical. Fractionation occurs because the strength of chemical bonds, between isotopes is different. Because heavy isotopes have greater mass, the chemical bonds between heavy isotopes have higher dissociation energies, the energy required to break a chemical bond. This means it requires slightly more energy to break the bond between a molecule with heavy isotopes compared to the same molecule composed of lighter isotopes. To use a common example from hydrology; it requires less energy to evaporate a water molecule with a H-H bond than it is to evaporate water molecule with an H-D bond (Figure 2.6).

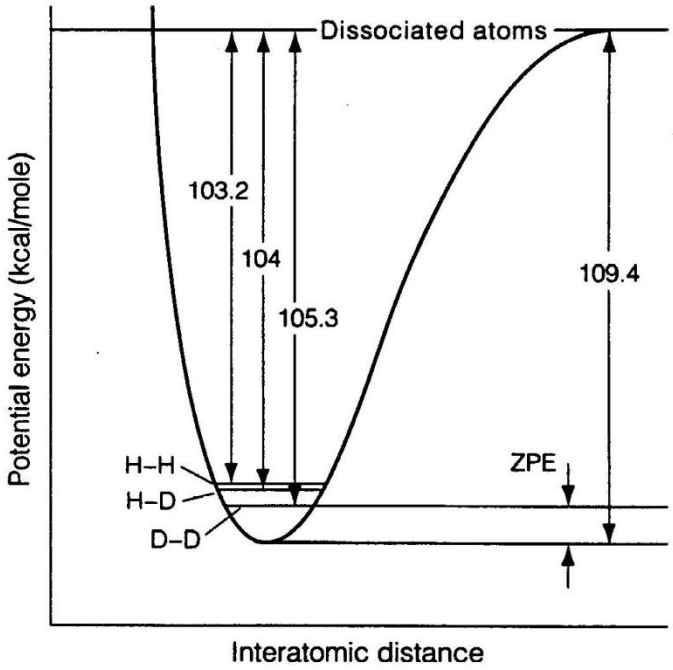

Figure 2.6 Potential Energy cure for diatomic hydrogen: As D-D bonds sit lower potential energy well than H-D and H-D it has higher dissociation energy. The result of this is a D-D bond is stronger than an H-H bond.

Rayleigh fractionation models fractionation in open systems where end member mass is progressively removed for the reservoir studied. Technically, equilibrium fractionation needs to occur in closed systems; however this is not the case for most hydrological systems studied. With Rayleigh fractionation condensation removes heavy isotopes from air vapor which is then loss as precipitation leaving behind air vapor depleted in ^{18}O and D. As this process continues, air masses and subsequent precipitation becomes progressively more and more depleted, and subsequently more and more negative in units of permil. Rayleigh fractionation is the cause of a number of observed effects in the hydrosphere, such as the continentality effect, where precipitation becomes isotopically lighter as the air masses move across continents.

2.3.6 The Meteoric Water Line

One fundamental empirical relationship observed in stable isotope geochemistry is the highly linear relationship between δD and $\delta^{18}O$ values in waters of meteoric origin (Figure 2.7). Friedman (1953), first reported this covariance between δD and $\delta^{18}O$ values, comparing his work with Epstein and Mayeda, (1953), and proposing mechanisms for isotopic fractionation in cloud dynamics (Sharp 2007). Craig (1961) published precise isotopic ratios for global meteoric waters and defined the global meteoric water line, GMWL (Equation 2.3).

$$\delta D = 8\delta^{18}O + 10$$

(Equation 2.3)

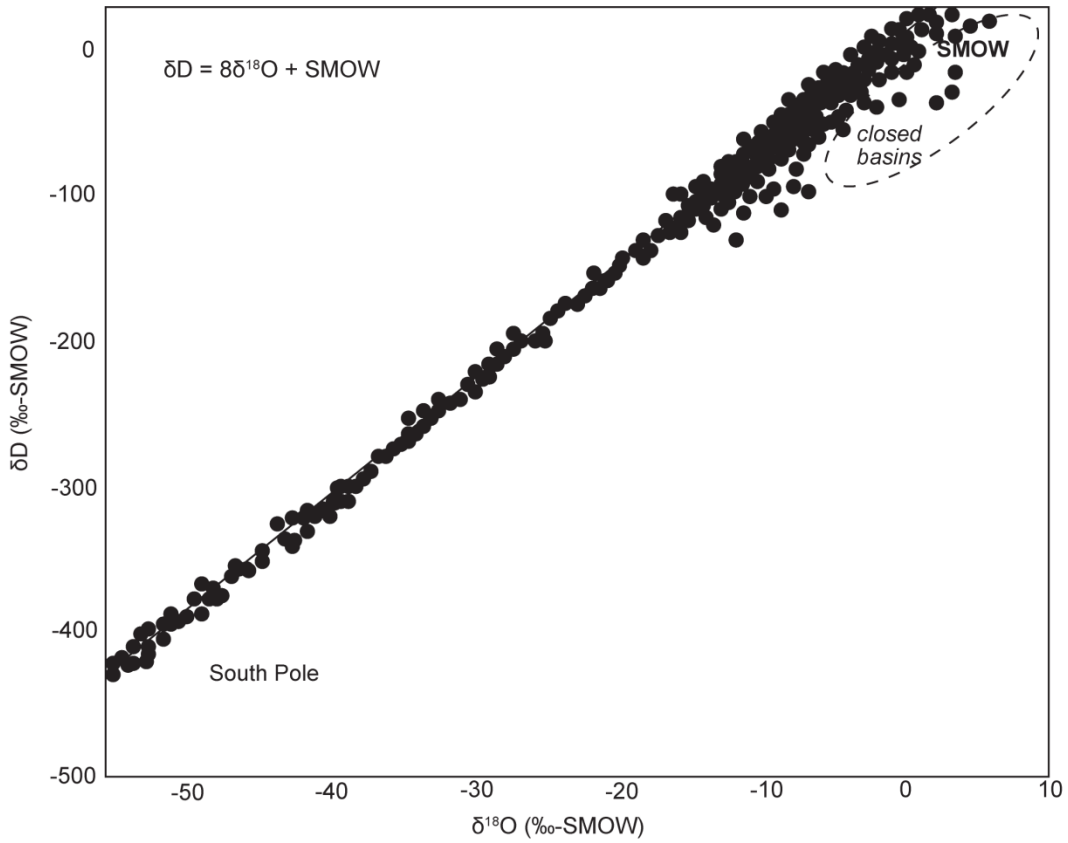

Figure 2.7 The global meteoric water line (Sharp 2007)

It is important to note that the standard SMOW, with δD and $\delta^{18}O$ values of 0 ‰, does not lie on the GMWL. This is because evaporation is a kinetic process, and the moisture being evaporated from the ocean is not in isotopic equilibrium with the ocean. The GMWL is in fact a weighted average of local meteoric water lines, LMWL, with slopes that are generally less than the GMWL slope of eight and have a variety of slope intercept values. The equation for the GMWL can be generalized for any point in earth's history, the slope of 8 remains constant but the intercept is variable (equation 2.4)

$$\delta D = 8\delta^{18}O + d$$

(Equation 2.4)

This parameter *d* is the deuterium excess parameter, coined by Dansgaard in 1964, and is often referred to as the deuterium excess (Sharp 2007).

2.3.7 Carbon Isotopes: background and fractionation

Carbon isotopes have a long history of being used in hydrological studies; most studies, however, have focused on the use of the radioactive isotope Carbon-14 for dating groundwaters. Carbon also has two stable isotopes, ^{12}C and ^{13}C, with ^{12}C being the most abundant. The carbon cycle is very complex and has been studied on a variety of spatial and temporal scales (Figure 2.8)**.**

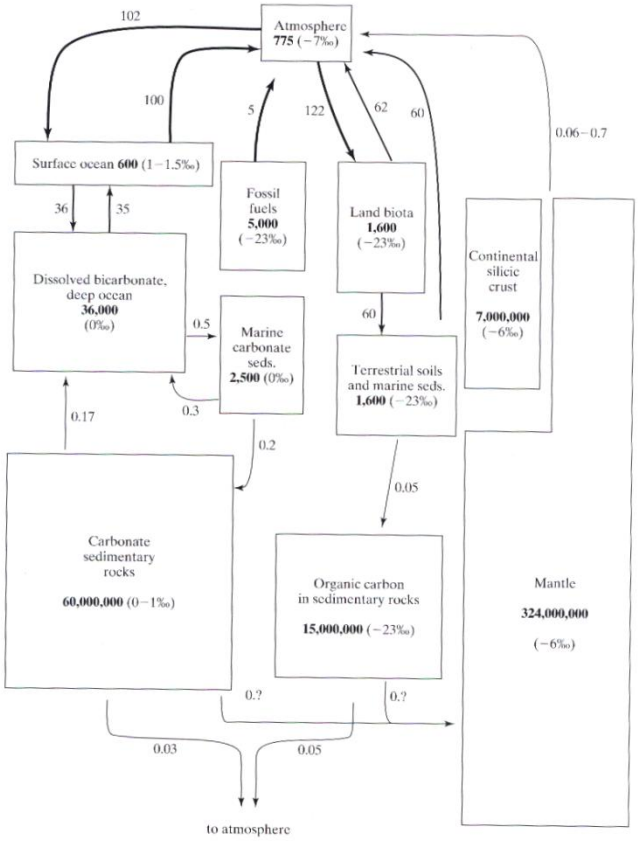

Figure 2.8 The Carbon Cycle: A conceptual model of the Carbon cycle showing amounts, fluxes and $\delta^{13}C$ values for each reservoir (Sharp 2007).

Research using carbon isotopes covers a large range of substances including organic and inorganic solids, gases and liquid phases along with a correspondingly large range of $\delta^{13}C$ values, from -40 to 10‰ (Figure 2.9)**.** Fractionation between inorganic carbon phases is relatively small, in contrast to fractionation between inorganic and biological organic carbon, e.g. photosynthesis. Plants can be divided into three photosynthetic categories, C3, C4, and CAM, which cause differing amounts of isotopic fractionation. Organically derived carbon is isotopically depleted in ^{13}C, ranging between $\delta^{13}C$ values of -26‰ (-22 to -30‰) for C3 plants and -12‰ (-20 to -9‰)for C4 plants.

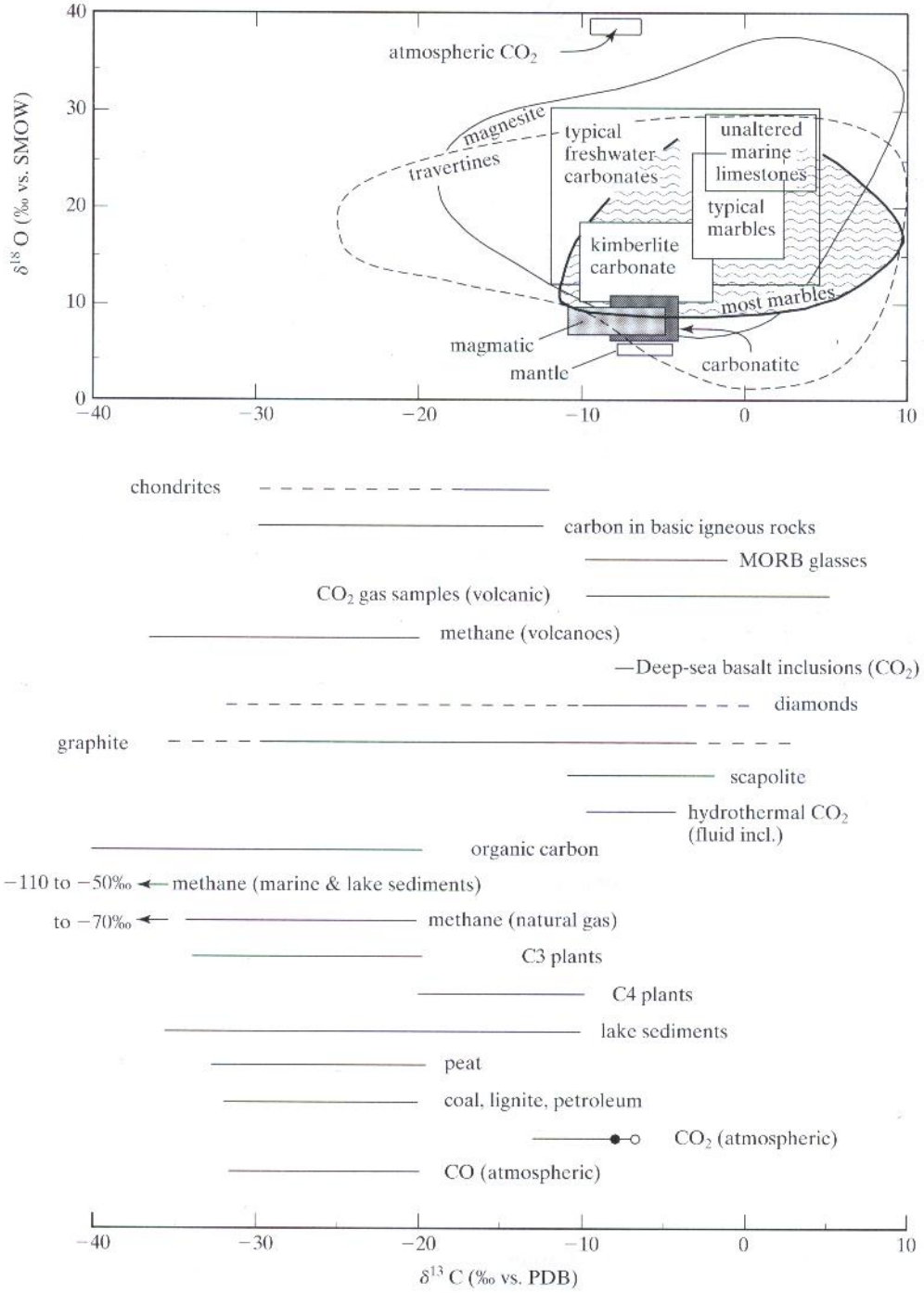

Figure 2.9 General ranges of $\delta^{13}C$, and $\delta^{18}O$, values for carbon-bearing materials (Sharp 2007).

2.3.8 Carbon Isotopes and hydrology

Studies using carbon isotopes in hydrology examine dissolved inorganic carbon (DIC) and dissolved organic carbon(DOC) to trace the carbon cycle through hydrologic systems. This section will focus on DIC; see also alkalinity section 2.4.2. DIC from the weathering of marine carbonate rocks has an ^{13}C enriched composition, compared to weathering of silicate rocks, which yields isotopic compositions related to soil CO_2 as a source of Carbon (Amoitte-Suchet et al. 1999). Riverine DIC has three main sources, dissolution of carbonate minerals, dissolution of atmospheric CO_2 and soil CO_2. The Average contribution of soil CO_2 to the DIC of rivers around the globe is estimated to be 67% (Berner et al 1983**,**Meybeck 1987, Amiotte et al 1995, Ludwig et al. 1996**)**. Quantifying carbon isotope fractionations in rivers is difficult, in a simple example, Amoitte-Suchet et al. (1999) found that groundwater and springs reflect the soil CO_2, including seasonal variation, while further downstream the river was relatively enriched in ^{13}C indicating isotopic equilibration of the aqueous CO_2 with atmospheric CO_2. (Amoitte-Suchet et al. 1999).

While much of the literature focuses on using carbon isotopes to determine the source of DIC, e.g. Aucour et al (1999), Gofiantini and Zuppi (2003), there have been a number of studies to use carbon isotopes of DIC as a tracer. Taylor and Fox (1996) used total dissolved inorganic carbon, TDIC, ^{14}C, and ^{13}C concentrations to trace groundwater-surface water interactions between the Waimakariri River and Christchurch Groundwater System, while Stewart et al 2012, used carbon isotopes, ^{14}C, and ^{13}C , as a compliment to other geochemical tracers to further refine models for these. Other applications of carbon isotope in hydrology include Haarstad and Maehlum (2012) who use ^{13}C from DIC to trace solid waste leachate from landfills in Norway, while Ettayfi et al (2011) used a wide array of geochemical and isotopic tracers, including carbon isotopes, to identify the origins and residence times of groundwaters in a carbonate aquifer in Morocco.

2.4 Geochemical tracers in Hydrology

2.4.1 Introduction

Water is known as the 'universal solvent'; thus it can have a wide number of dissolved substances in it. This dissolve load can be used to quantify the water quality, and ultimately water origins. Water can dissolves substances in a number of ways. Atmospheric carbon dioxide dissolves in water forming carbonic acid which in turn interacts with rocks and minerals through weathering reactions. Water flowing through soils can pick up dissolved substances from both the soil as well as biological activity of microbes in soils. Anthropogenic activities, including but not limited to farming, industry, waste disposal,

and effluent processing, have the potential to interact with water adding to dissolved load. In the hydrological sciences aqueous geochemistry can provide insight into the origins of these dissolve loads and trace waters evolution through the hydrosphere. This section focuses on anions, as these are the only complimentary tracers related to this thesis.

2.4.2 Ions

An ion is simply an atom or molecule where the numbers of electrons are not equal to the number of protons resulting in either a net positive or negative charge. Cations are ions with net positive charges, while anions are ions with net negative charges.

2.4.3 DIC and Alkalinity

Alkalinity is a measurement of the buffering capacity of a solution and is used to calculate the DIC, dissolved inorganic carbon, in a solution. DIC is composed of aqueous carbon dioxide (CO_2(aq)), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. It is generally assumed that the concentrations of aqueous carbon dioxide are nearly identical to carbonic acid (Drever 1997, *Stumm and Morgan, 1981*). The concentrations and activities of each species in solution depends on a number of factors, primarily pH, but also the partial pressure of CO_2 (pCO_2) and temperature (Figure 2.10).

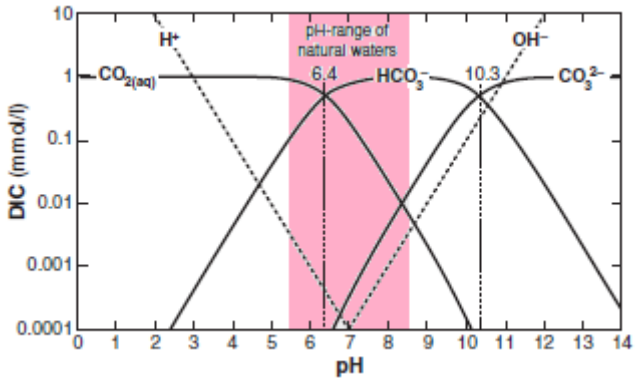

Figure 2.10 Concentrations of DIC species as a function of pH (Bjerrum plot) for freshwaters at 25°C (modified from Drever 1997)

When gaseous CO_2 is brought into contact with water, the CO_2 will dissolve, forming carbonic acid H_2CO_3, until equilibrium is reached. This process is shown in equation 2.5:

$$CO_{2(gas)} + H_2O \leftrightharpoons H_2CO_3$$

(Equation 2.5)

Depending on solution pH, temperature and pCO_2, the H_2CO_3 will dissociate into hydrogen and bicarbonate ions as shown by equation 2.6.

$$H_2CO_3 \leftrightharpoons H^+ + HCO_3^-$$

(Equation 2.6)

DIC in most surface water bodies is comprised primarily of bicarbonate (HCO_3^-) ions, which can have three distinct origins, soil CO_2, and the weathering of carbonate or silicate rocks. In carbonate weathering, half the produced DIC originates from the carbonate mineral and half from aqueous CO_2 (Equation 2.7).

$$CaCO_3 + CO_2 + H_2O \leftrightharpoons Ca^{2+} + 2HCO_3^-$$

(Equation 2.7)

Weathering of carbonate minerals occurs with other acids, such as sulfuric acid, the carbon in the DIC will originate solely from the carbonates (Equation 2.8).

$$2CaCO_3 + H_2SO_4 \leftrightharpoons Ca^{2+} + 2HCO_3^- + SO_4^{2-}$$

(Equation 2.8)

In weathering of silicates, such as albite, DIC originates solely from dissolved carbon dioxide (Equation 2.9).

$$2NaAlSi_3O_8 + 2CO_2 + 3H_2O \leftrightharpoons Al_2Si_2O_5(OH)_4 + 2HCO_3^- + 4SiO_2$$

(Equation 2.9)

Alkalinity, measured in milliequivalents per liter, mEQ/L, is the ability of a solution to neutralize acids. Total akalinity is the sum of all bases, e.g carbonate, bicarbonate, organic acids, borate, which are titratable with strong acid. In most natural waters anions such as borate, ionized silicic acid, bisulfide, and organic ions are only present in small concentrations compared to bicarbonate and carbonate, therefore alkalinity is effectively the total carbonate alkalinity, the sum of bicarbonate and carbonate anions in solution.

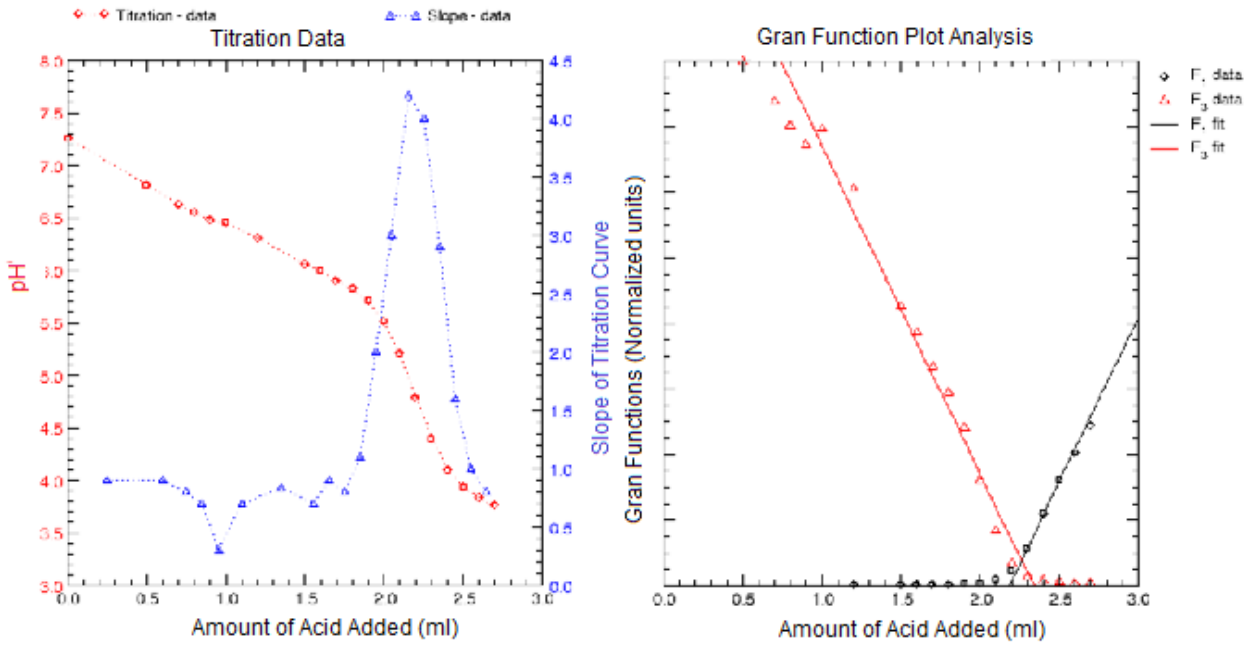

Figure 2.11 A alkalinity titration and Gran Plot Analysis

Alkalinity is determined in the field by titration (Figure 2.11). Titrations are carried out by adding a strong acid at fixed molarity, such as sulfuric acid, to the solution and measuring the changes in pH, with the buffering capacity of the solution until the equivalence point is passed. The equivalence point is the point where all of the bicarbonate has been neutralized and acid added after this point will rapidly drop the solutions pH. Traditionally alkalinity titrations were carried out until the pH was approximately 4, however for greater accuracy pH is now measured until it is clear the end point has been past, i.e. a change of less than .1 pH when measured using a pH electrode. The shape of a titration curve is determined by the buildup of H^+ as acid is added and the logarithmic relationship between hydrogen ion concentration and pH. Titrations are analyzed using a Gran titration analysis, otherwise known as a Gran plot, which provide the most accurate measurement of alkalinity from a titration curve (Stumm and Morgan 1991, Drever 1997).

2.4.4 Chlorine

While there are several oxidized states of the element Chlorine, Cl, the chloride form, Cl^- is the only one which is significant in surface waters. Chlorine is extremely soluble, and in the ocean, chloride, accounts for more than three-fourths of the total amount of chlorine in the outer crust, atmosphere, and

hydrosphere (Hem 1985). Chloride is a very conservative geochemical tracer as chloride ions do not significantly enter into oxidation or reduction reactions, form no important solute complexes with other ions unless at extremely high concentrations, do not form salts of low solubility, are not absorbed on mineral surfaces and have limited biochemical interactions. Chloride is present in all natural waters, but generally concentrations in most surface waters are low. Chloride values in inland meteoric waters are low, but precipitation near the ocean can range from one to several tens of milligrams per liter.

2.4.5 Bromine

Bromine in natural waters is always present as the bromide ion, Br^-, and is a conservative tracer similar in chemical behavior to chlorine. In freshwaters bromide generally is present only at very low concentrations with concentrations in meteoric waters ranging from 5 to 150 micrograms per liter; however it can be a significant solute in geothermal waters (Hem 1985). Bromide used in conjunction with chloride can be a powerful tracer by examining the chloride/bromide ratio. Davis et al. (1998) summarized the use of chloride bromide ratios in potable groundwaters and established observed ratios for various water sources, e.g. shallow groundwater, domestic sewage, atmospheric.

2.4.5 Nitrogen

The behavior of nitrogen in aqueous solution is heavily influenced by biological processes. Nitrogen gas (N_2), is changed into an oxidized state mainly through biological fixation, though anthropogenic inputs into the nitrogen cycle through the production of fertilizer has become a significant input to this system. Nitrogen occurs in waters as nitrite or nitrate anions (NO_2^-, NO_3^-), and the cation ammonium (NH_4). Nitrate is readily soluble in water and is generally chemically stable over a wide range of conditions, while nitrate is unstable in aerated water and indicative of anaerobic conditions and is often an indicator of pollution from sewage or organic waste (Hem 1985). High concentrations of nitrate, in excess of 44 mg/l NO_3^- ,can cause methemoglobinemia in children and the elderly. Fertilizers and livestock are major inputs of nitrate into groundwaters and surface waters, and nitrate concentrations exceeding 10mg/l are common on small to medium sized rivers in agricultural areas (Hem 1985).

2.4.6 Sulfur

Sulfur occurs in oxidation states ranging from S^{2-} to S^{6+} and its chemical behavior is strongly linked to the redoox properties of aqueous systems. Sulfur In the scope of this thesis is limited it its most oxidized form Sulfate anion (SO_4^-). Sulfur has a number of sources and its geochemical cycle is characterized by rapid recycling of solute forms between water and the atmosphere. Sources for sulfur in freshwaters

include rock weather, biological processes, and anthropogenic activities, both as a direct source in runoff and by releasing sulfur into the atmosphere.

Chapter 3: Regional Geology/Study area

3.1 Introduction

This chapter introduces the study area and its broader geologic context. It starts with an introduction to the study area, the Avon and Heathcote rivers, and the region's geographical context in the central Canterbury plains. The second section, presents an over overview of the regional tectonic setting, bedrock geology and recent (2010 – 2012) seismic activity. The third discusses the surficial geology of the Central Canterbury Plains and Christchurch area followed by an overview of the hydrology of the Christchurch Groundwater System (CGS).

3.1.1 Study Area

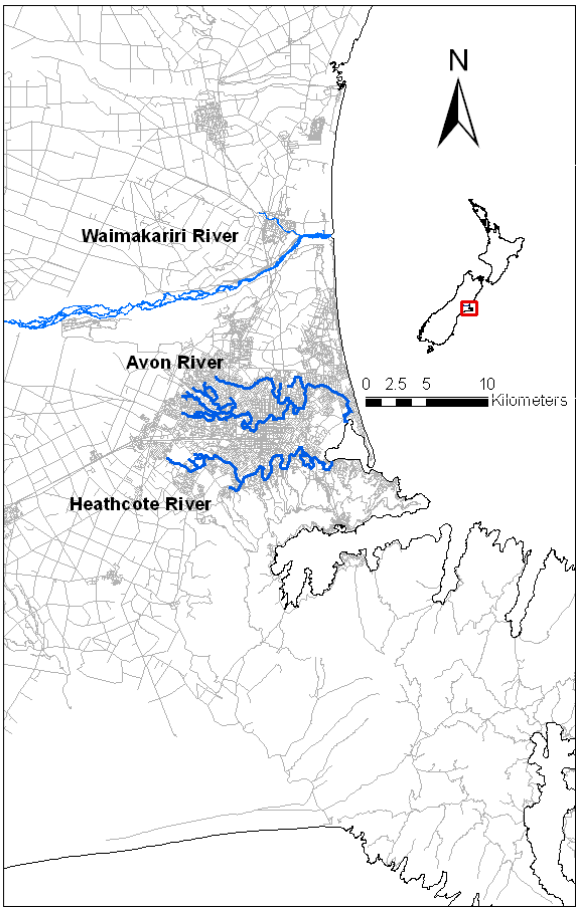

Figure 3.1 Study Area

The study area for this thesis is the Avon-Heathcote River System, located in the city of Christchurch, New Zealand (Figure 3.1). The Avon and Heathcote rivers are both lowland spring-fed rivers that are intimately linked to the Christchurch Groundwater System (CGS), and act as the primary surface-water drainage systems for the metropolitan Christchurch area. Christchurch is located on the eastern coast of New Zealand's South Island, and is situated along the eastern margin of the Central Canterbury Plains. The Central Canterbury Plains are part of the larger Canterbury Plains, New Zealand's largest alluvial sedimentary system.

3.2 Bedrock Geology

3.2.1 Tectonic Setting

The South Island of New Zealand is located on the active tectonic plate boundary between the Indo-Australian and Pacific plates (Figure 3.2). The ongoing Kaikoura Orogeny, which began ~25 Million years ago, is the result of oblique convergence between these two plates, causing the rise of the Southern Alps with the Pacific plate being up-thrust over the Indo-Australian Plate. This convergence is manifested as the Alpine Fault, a >650 km right lateral dextral fault (Koons 1989, Koons 1990). Currently the rate of uplift varies between 8-10 mm/yr adjacent to the Alpine fault, though uplift rates have varied in the past with uplift accelerating in the past 5 million years. (Tippit and Kamp 1995, Little et al. 2005).

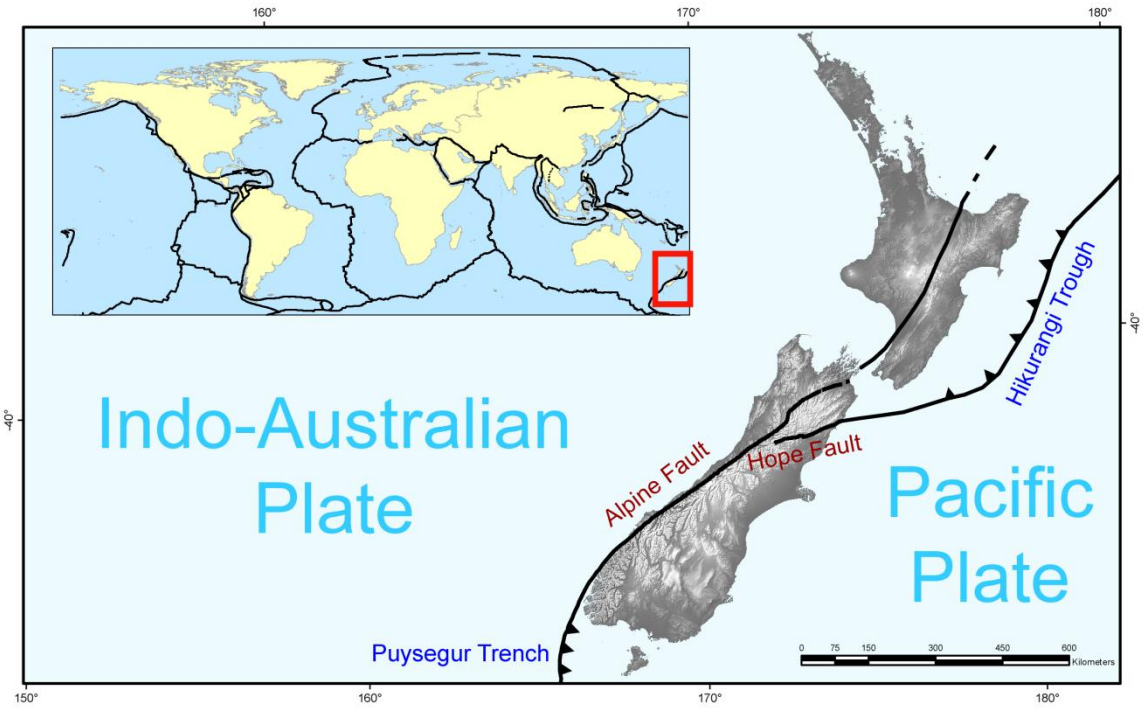

Figure 3.2 New Zealand's tectonic setting (used with permission from Blackstock 2011)

3.2.2 Basement Geology

For much of its pre-Kaikoura Orogeny history, the majority of the Zealandia micro-continent was below sea level. The predominant bedrock unit in the Canterbury Plains system is the Torelesse Supergroup. The Torelesse Supergroup consists mainly of partially metamorphosed greywacke, which is Permian to Jurassic in age (Brown and Weeber 1992). Torelesse Greywacke in Canterbury is comprised of a structurally complex geosyncline with ridges and troughs (Hicks 1989). While Torelesse Greywake is the basement rock for much of the study area, the basement and sediment of the southern study area is intruded upon by Banks Peninsula, an extinct Miocene aged intraplate basaltic complex composed of basalt and trachytic lithologies (Brown and Weeber 1992).

3.2.3 Recent Seismic Activity

The Alpine Fault accommodates approximately 50-80% of New Zealand's 37 ± 2 mm yr^{-1} motion of the plate boundary, with the rest of the strain being taken up by various faults in the South Island, most notable through Marlborough Fault Zone **(**Berryman et al 1992, DePascale G.P. 2012)**.** In the early morning hours of September 4th, 2010 a M_w 7.1 earthquake, the Darfield earthquake, occurred on a previously unknown fault, the Greendale Fault. This earthquake was located 44 km west of Christchurch's central business district (CBD) and at a depth of 11km. The Darfield earthquake has produced a prolonged series of aftershocks termed the Christchurch Sequence; among these was the February 22nd, 2011 earthquake, a M_w 6.2 aftershock located 10 km southeast of the CBD that killed 185 people and causing a estimated US $10 billion worth of damages or more (Quigley et al 2011) (Figure

3.3*)*. Damages included loss of life, widespread liquefaction in both earthquakes, as well as during another significant aftershock in mid-June 2011, damage to sewer lines and water supplies, and widespread infrastructure damage, especially to heritage buildings, residential high-rise buildings and roads.

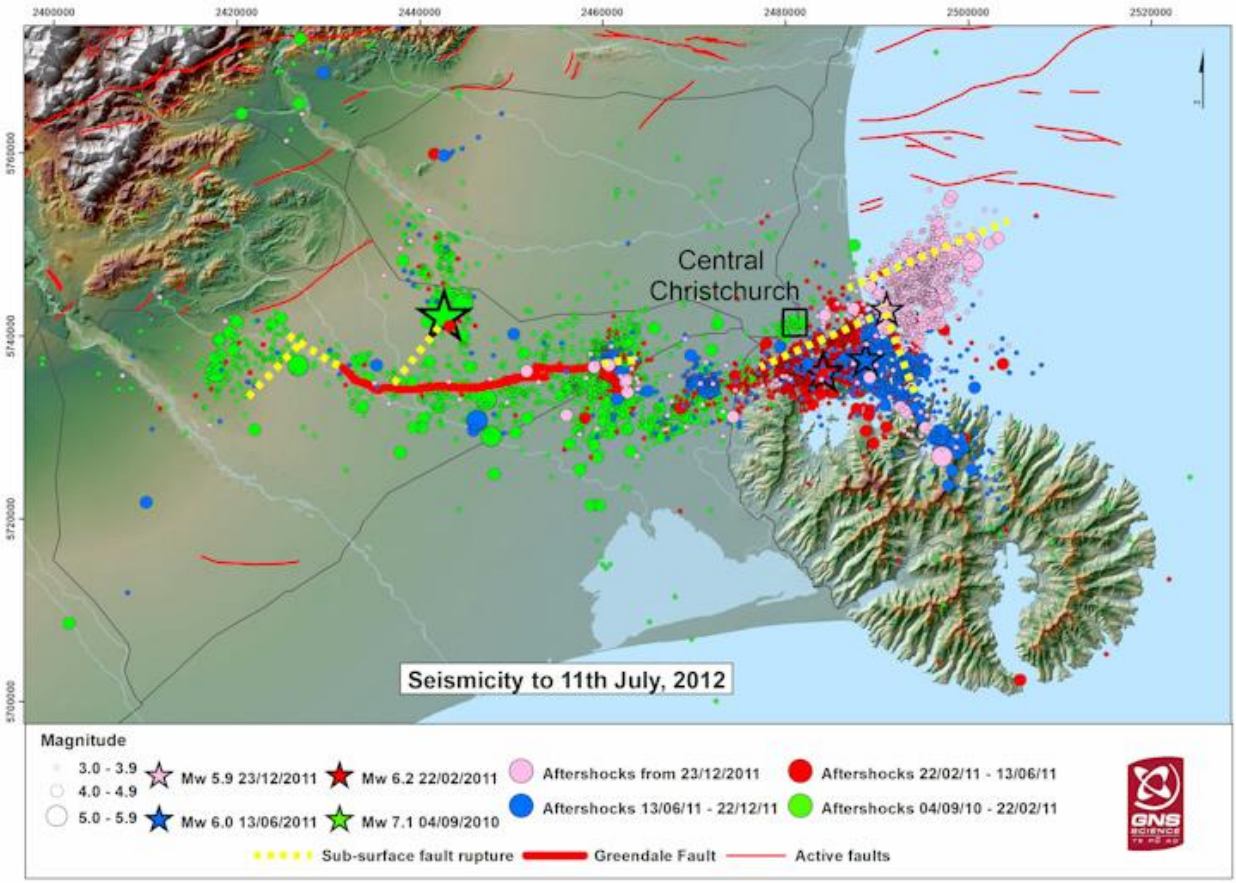

Figure 3.3 Darfield Earthquake and Christchurch Aftershock Sequence (GNS Website)

3.3 Surficial Geology

3.3.1 Surface Geology

The Central Canterbury Plains are New Zealand's largest alluvial sequence, encompassing an area roughly 8000 km^2 between the Southern Alps and the Pacific Ocean. The Central Canterbury Plains is the area bounded by the Waimakariri River to the north and Rakaia River to the south (Lekie et al 2003) (Figure 3.4). Morphologically the Central Canterbury plains are gently graded abandoned flood plains, which were last active and flowing west to east during the Last Glacial Maximum (LGM) (Figure 3.5). In the foothills of Southern Alps, the Rakaia and Waimakariri rivers have formed deep terraced canyons, from post glacial entrenchment. Incision rapidly decreases away from the foothills with occupied or recently abandoned Holocene floodplains near the coast (Forysth et al 2008).

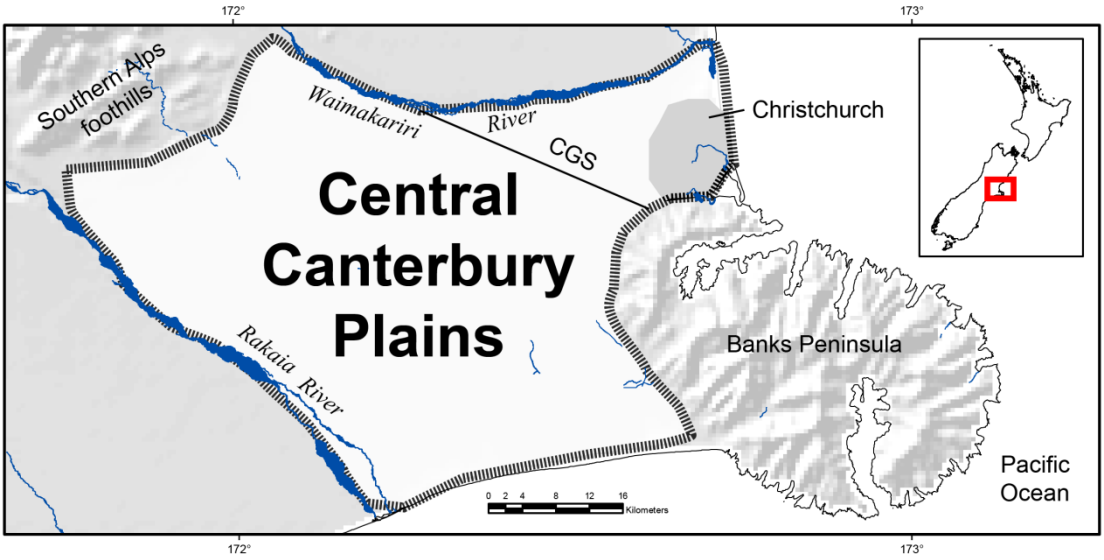

Figure 3.4 The Central Canterbury Plains (used with permission from Blackstock 2011)

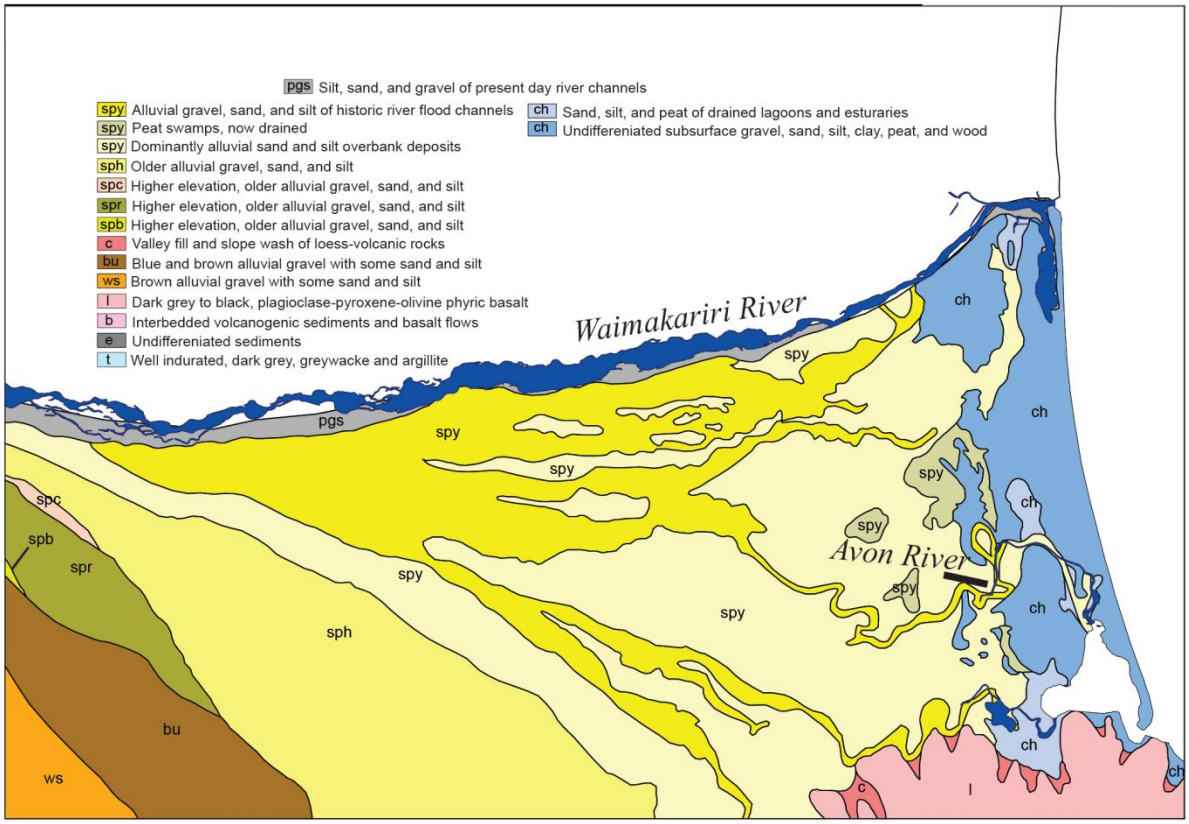

Figure 3.5 Surface Geology of the North Central Canterbury Plains including Christchurch (Modified from Brown and Weeber 1992)

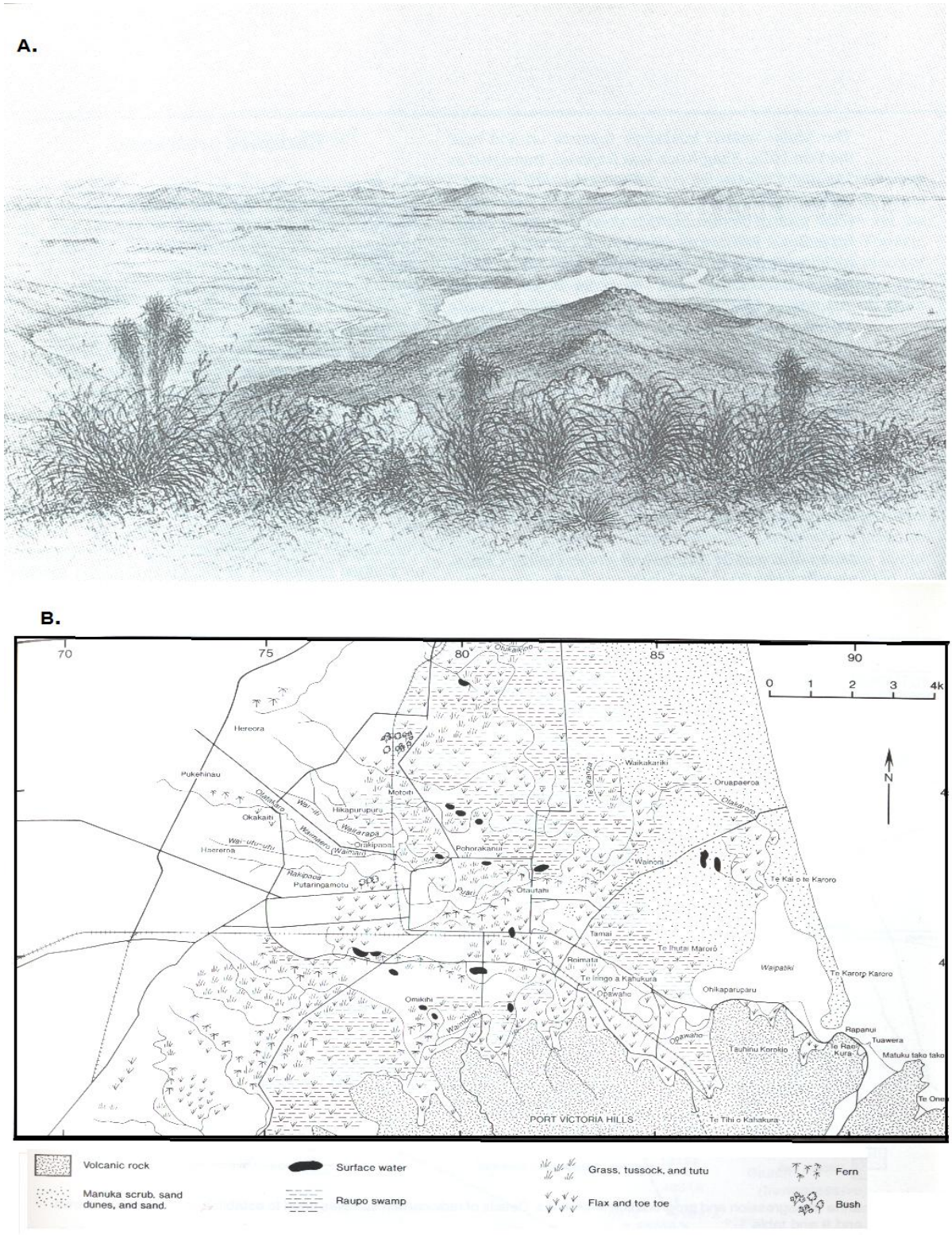

Figure 3.6 Sketch of Christchurch from 1854: looking north from the Port Hills A) Drawing from an Early Settler B) Christchurch Circa 1856 adapted from "black maps" (Modified from Brown and Weeber 1992)

The landscape of Christchurch, since its establishment in 1850, has been dramatically altered by human activity. The city is coastal and low-lying and was originally an area of swamps, marshes and estuaries protected by coastal sand dunes (Figure 3.6). Human activity has all but erased this original landscape with extensive draining and infilling of swamps, with industrial, commercial and household rubbish, and by leveling of much of the lowland topography, such as sand dunes (Brown and Weeber 1992).

The Canterbury Plains are a series of coalescing alluvial fans laid down by braided rivers, in particular the Waimakariri River, which flows east from the Southern Alps. The Canterbury Plains are predominately comprised of glacio-fluvial outwash laid down in gravely layers interspersed with sand to silt sized layers, representative of changes in the depositional environment (Brown and Weeber 1992, Leckie 2003). These gravels have been deposited in the last 5 Ma, during the late Tertiary and Quaternary, with deposition of gravels occurring primarily during glacial periods. The thickness of the alluvial sequences varies across plains due to the complicated nature of the underlying bedrock structure, but on average is 380 to 600m thick (Talbot et al 1986, Hicks 1989, Brown and Weeber 1992). Inland correlation between sedimentary sequences in the Canterbury Plains is difficult to establish as marker beds are rare (White 2009, Forysth et al 2008). Towards the coast, distinguishable alternating sequences of glacial fluvial outwash and interglacial marine sediments are observable to a depth of 280m and form the geologic framework for the CGS (Brown and Weeber 1992, Forysth et al 2008**)**.

3.3.2 Hydrogeology of the Christchurch Groundwater System

The Christchurch Groundwater System (CGS) is the sole source of water for Christchurch, and extremely valuable resource as groundwater is of sufficient quality that no treatment is necessary prior to distribution. The CGS is categorized by highly permeable glacio-fluvial gravels interfingered with impermeable interglacial marine sediments and by semi-confined to unconfined gravel aquifers in the westernmost portion of the study area (Figure 3.7). As groundwater moves from the unconfined and semi-confined aquifers in the east to the confined aquifers in the west, artesian pressure develops; hence the CGS is often referred to as the Christchurch Artesian Aquifer system.

The CGS is comprised of at least five artesian aquifers, with water pressures increasing with depth. Despite long-term monitoring of the CGS, flow paths from between aquifers as well as the hydrological significance of aquitards at depth, remain uncertain and the subject of major discussion (Talbot et al 1986, Brown and Weeber 1992, White 2009, Stewart 2012). This uncertainty is in part due to the heterogeneous nature of this aquifer; yet, despite this heterogeneity, regional and local flow paths can be discerned (Talbot et al 1986, Brown and Weeber 1992, Stewart et al 2002, Stewart 2012). For instance, upward leakage from the deeper aquifers into the shallower aquifers, due to the increased vertical hydraulic gradient with depth, has been documented in geochemical monitoring of the CGS (Brown and Weeber 1992, Stewart 2012).

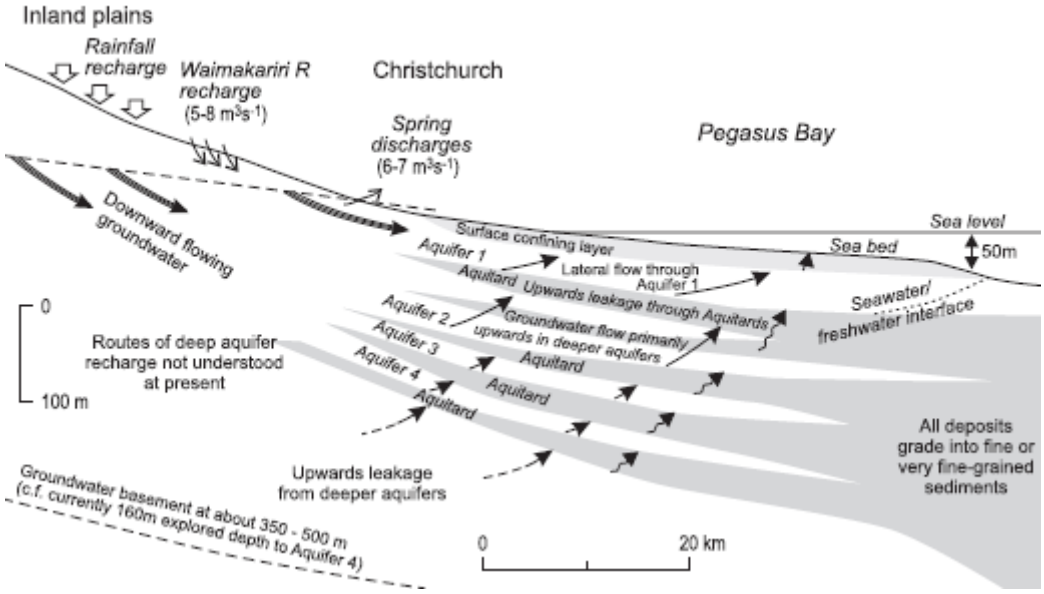

Figure 3.7 Christchurch Groundwater System with estimated recharge amounts (Stewart et al 2012)

Recharge for the CGS is thought to come largely from the Waimakariri River, in the Halket area, with some recharge being provided by the Central Canterbury Plains (Talbot et al 1986, Brown and Weeber 1992, Stewart et al 2002, Hanson and Abraham 2009, Stewart 2012). The flow to the CGS from the deeper Central Canterbury Plains aquifers is not fully understood at present, once again due to the heterogeneous nature of these aquifers (Stewart 2012). Stewart (2012) recently summarized and expanded on 40 years of physical and geochemical research incorporating the works of Talbot and others (1986), Taylor and others (1989), Taylor and Fox (1996), Hanson and Abraham (2009), among others. During the past 40 years the mean ages for the deep aquifers have changed dramatically in response to continuous and increasing water extraction. Testing in the 1970s showed young mean ages of 60 to 70 years across the city. This was interpreted as lateral inflow of young Waimakariri sourced water. Later sampling has shown an increase in the mean age across the aquifer which indicates an up flow of older water from depth, likely sourced from deeper aquifers recharged from the inland Central Canterbury Plains. As of 2006, there was a sharp age gradient in waters across Christchurch from east to west, from 300 to 1400 years. Stewart, 2012, interprets this gradient to mean that a large body of much older water exists on the seaward side of system, where deep aquifers are blind, and that this body can continue to yield high quality water for many years; though continued abstraction from the CGS will likely cause the deep aquifer water to be replaced or bypassed by younger groundwaters sourced from the Waimakariri River and Central Canterbury Plains (Stewart 2012).

3.3.3 The Avon and Heathcote Rivers

The Avon and Heathcote Rivers, the Otakaroro and O-pa-waho respectively in Maori, are both lowland spring fed streams originating in the western portion of Christchurch. These rivers occupy former channels of the Waimakariri River and empty into the Avon-Heathcote estuary (Figure 3.8). The Avon

River used to discharge to the sea near Travis Swamp but southward progradation of the Brighton Spit forced the river into its current position between 500 and 2000 years ago (Deely 1991). For more information on the formation of the estuary, Finlay and Kirk (1988) and Deely (1991) provide detailed descriptions.

Combined the rivers have a catchment of 188 km^2 which covers and drains most of urban Christchurch (Figure 3.8) (Canterbury Regional Council Report 1992). The catchment for both rivers has been greatly modified by human development with the establishment of Christchurch. Wetlands and swamps have been filled and drained and stop banked to prevent flooding (Canterbury Regional Council Report 1992, Brown and Weeber 1992). The Avon's catchment is comprised almost entirely of flat urban land, while the Heathcote's catchment is mostly flat but also contains the northern slopes of the Port Hills, which are only partially developed with swaths of undeveloped areas of pasture and forestry.

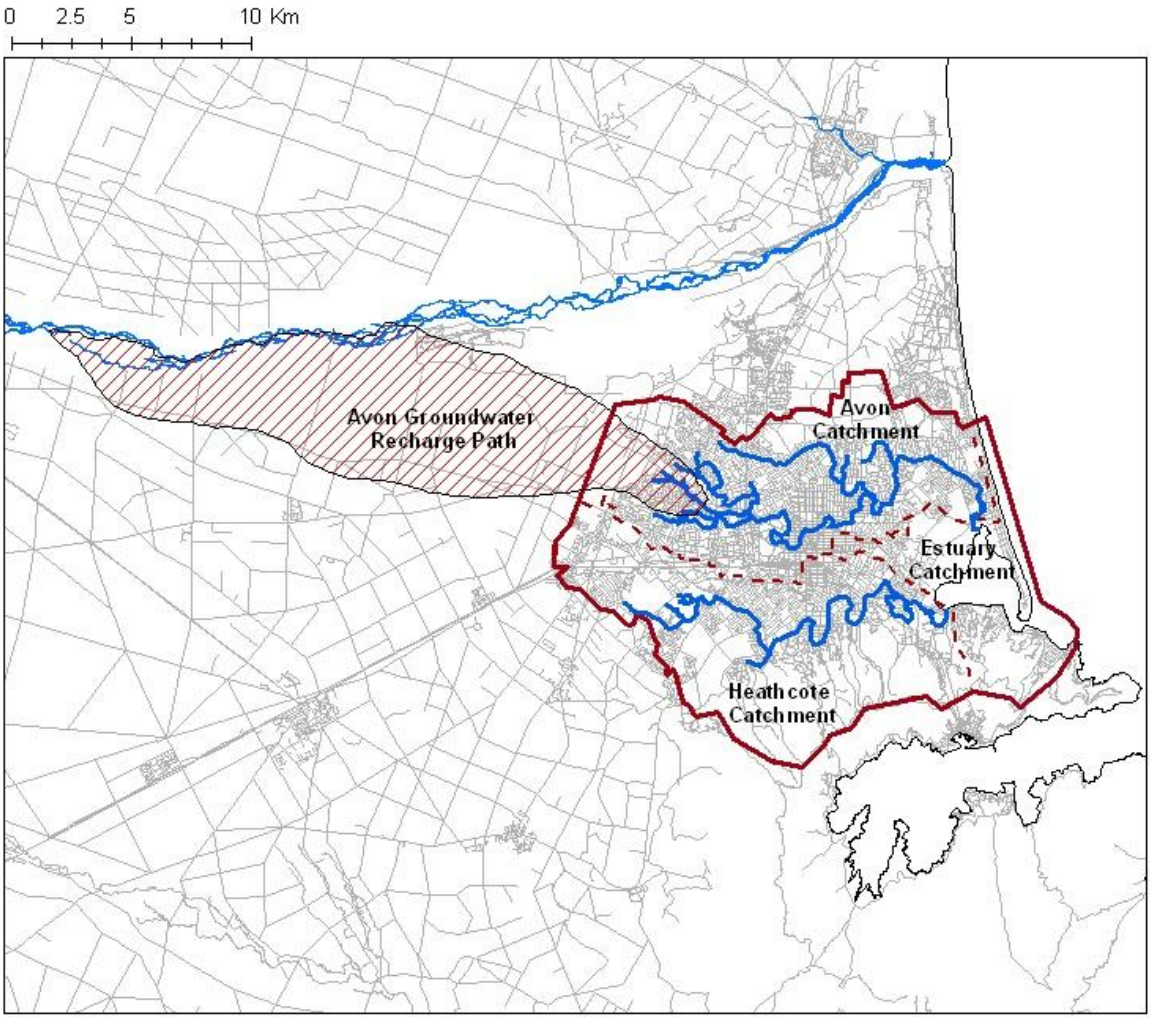

Figure 3.8: Catchment of the Avon and Heathcote Rivers (Modified from Canterbury regional council report 1992 and White 2009).

The Avon and Heathcote Rivers originate from a series of depression springs near the unconfined-confined boundary in the Western portion of the CGS (Cameron 1992, White 2009). Flows for both rivers are dominated by groundwater and the rivers are well sustained even during very dry summer periods. For example, it was estimated that a land area of ~261 km^2, significantly larger than the actual catchment, is required to support the estimated baseflow for the Avon River (Cameron 1992). The Avon River has a median base flow of 1679 L/s, while the Heathcote median discharge is 753 L/s (Cameron 1992, McKerchar 2001). In the Avon and Heathcote, storm runoff comprises only a minor portion of total annual flow. There is season fluctuation in discharge with the highest flows occurring in winter, from July through November, with the lowest flows occurring generally in January and February. White (2009), using well logs and groundwater flow paths for the CGS, constructed a catchment model for groundwater recharge to the Avon River (Figure 3.9) (White 2009). The Heathcote River also originates from depression spring at the Western Boundary of the CGS. The source of these springs and the water feeding them has received relatively little detailed study, though it is also thought to be recharged by groundwaters sourced from Waimakariri.

3.4 Climate

The South Island of New Zealand, owing to its mid-latitude location, is situated in the circumpolar westerly wind belt, which produces considerable variability in weather (Struman and Trapper 1996). At 43.5^o latitude, Christchurch is in the 'roaring forties', and its climate is milder than many other locations at similar latitudes due to its maritime climate. Weather in Christchurch is dominated by a sequence of depressions and anticyclones moving west to east, in the predominantly westerly airflow (Struman and Trapper 1996). The Canterbury Plains receive between 600-800 mm yr^{-1} with higher rainfall amounts towards the coast, as well as at higher elevations on Banks Peninsula, and within the foothills of the Southern Alps (Tomlinson, 1992). Total annual pan evaporation varies between 1271 to 1329 mm with moisture deficiates occuring during summer months (Trewinnard and Tomlinson 1986). Precipitation events tend to be evenly space over time, though there is a slight autumn-winter maximum (Tomlinson, 1992).

Chapter 4: Methodology

4.1 Introduction

In an effort to characterize the geochemical composition of the Avon-Heathcote river system, a total of 49 samples were collected from the Avon, Heathcote and Waimakariri Rivers at roughly quarterly intervals. Samples were analyzed for pH and alkalinity in the field and stable isotope and anion compositions at the University of Canterbury. Altogether, 27 samples from the Avon, 14 samples from the Heathcote and 2 samples from the Waimakariri Rivers were collected. In addition to this, 34 precipitation events, and 3 samples from the Okeover were also collected opportunistically. An additional 98 surface water samples were collected for stable isotope and anion analysis in the 15 days following the February 22nd, 2011 Christchurch earthquake. This Chapter describes the in-field and laboratory methods used for site selection, sample collection, handling, and analysis. Sampling locations and the reasons behind their selection are presented, first. Second, the methods pertaining to field sampling and in field processing of sampling, including alkalinity titrations are presented. Finally the methods associated with anion and isotopic determinations are presented.

4.2 Sites and Site Selection

Seven sampling locations were selected along the Avon River, while six sites were selected for the Heathcote River and a single site was selected for the Waimakariri River (Figure 4.1). For the Avon and Heathcote, the sampling locations were selected at relatively equidistant along the main stem from the estuary (i.e. mouth) to headwaters, while also trying to locate sites at or between major confluences. The sites were also selected for ease of access and safety. Only one Waimakariri site, off a boat ramp near state highway 1, was selected for sample due to safety concerns and limited river access points.

Following the February 22nd earthquake, samples were collected for analysis from Rivers, lakes, and springs (figure 4.2). Due to limitations in site access and the difficulties sampling immediately following a major disaster the majority of River samples came from the Avon River. Samples were taken from five sites along the Avon River, with two samples from the Heathcote River and single sample from the Waimakariri River. These sites are close to, and overlap, the sites selected for quarterly sampling. Lake samples were collected, Lake Victoria and Lake Abbet, both fed by groundwater bores and located in Hagley Park and the lake in the Canterbury Agricultural Park. Spring samples were collected around the city at liquefaction sites and surface springs which appeared following the February 22nd earthquake.

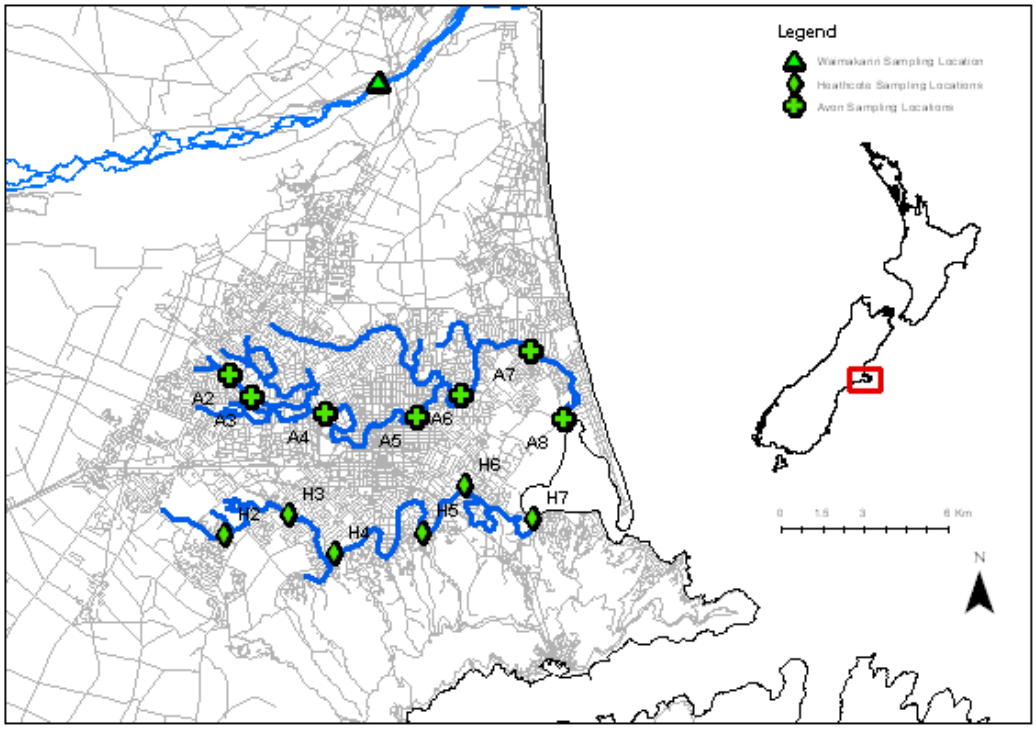

Figure 4.1 Sampling locations for the June 2011 to February 2012 sampling period

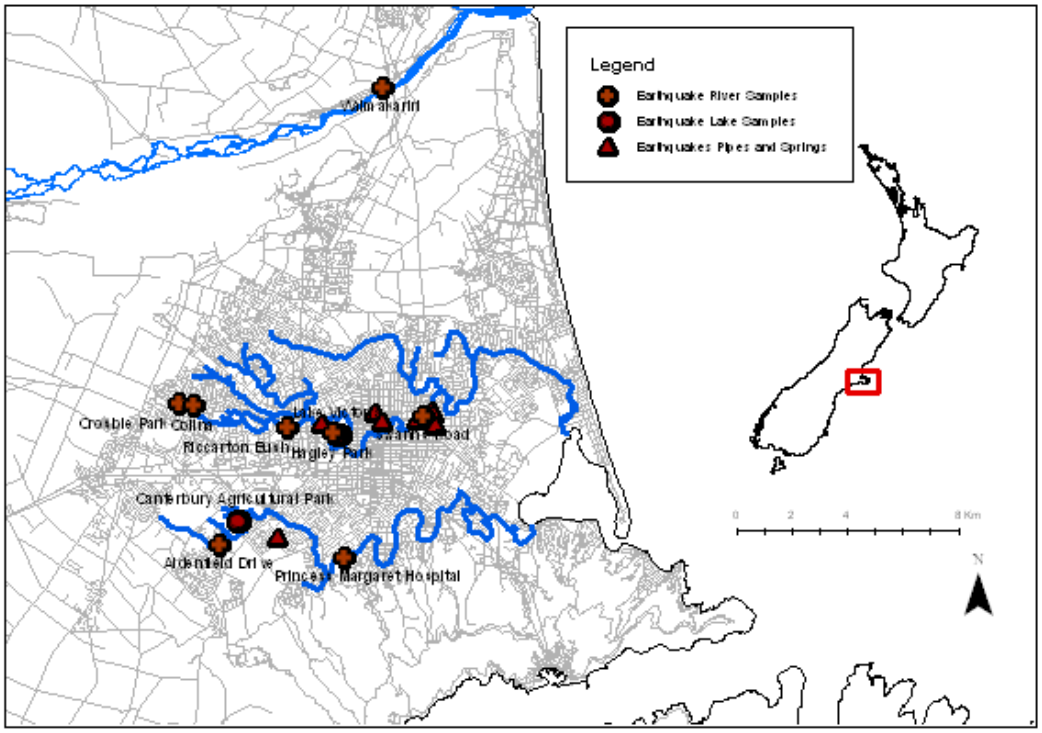

Figure 4.2 Sampling locations following the February 22nd earthquake (February 2011 to March 2011)

4.3 Sample Collection and Field Processing

Sampling was carried out in 4 discrete periods in June, September, October 2011 and February 2012. (figure 4.3). The aim of this protocol was to collect three samples representing the winter, spring and summer seasons. The October 2011 sampling occurred only on the Avon River, and was an opportunistic sampling specifically targeting geochemical conditions during a major storm event, in this case a large southerly storm. The Heathcote was not sampled during this storm, as associated flooding made access to sampling sites unsafe. The rain samples were collected optimistically during large precipitation events during the sampling period. The total number of samples collected and dates of collection are located in table 4.1.

Site	Sample Total	Jun-11	Sep-11	Oct-11	Feb-12
Avon	27	7	7	6	7
Heathcote	14	4	6	0	4
Waimakariri	2	0	1	0	1
OkeoverStream	3	1	0	2	0
Rain	34				

Table 4.1 Sampling Totals

In the course of sampling a number of challenges arose resulting in some sites, mostly on the Heathcote, being omitted. For instance, supplies of .45 µm filters ran out in the June 2011 and February 2012 sampling periods, resulting in missed sites along the Heathcote and being unable to sample the Waimakariri altogether in June 2011. Earthquake damage, repairs, and flooding also resulted in sites being periodically inaccessible during planned sampling trips.

River samples were collected from bridges, both road and pedestrian, using a weighted bottle sampler wherever possible. In the June 2011 sampling period a bucket with a weight on it was used to collected samples and a weighted bottle sampler was used for the remained of the sampling. The sampling procedure is as follows; the weighted bottle sampler was given three native rinses, then the collected water was poured into a 100 ml container which was also given 3 rinses. For δD and $\delta^{18}O$ analysis, water was taken from the 100 ml container using a 10ml syringe, which was flushed 3 times with native water, and filtered using a 0.45µm filter into a 50 ml test tube, that was also rinsed three times with filtered water. Test tubes holding samples for isotopic and anion analysis were filled to the brim and sealed to prevent evaporation in the headspace. For $\delta^{13}C$-DIC analysis ~3ml of filter water was injected into a helium filled vial with ~100µl of 103% phosphoric Acid (after Spotl, 2005). Rain samples were collected at the University of Canterbury. The rain samples were filtered using a 0.45µm filter and put into a 50 ml test tube that was rinsed three times with filtered water for stable isotope analysis.

Figure 4.3 Avon River locations, June 2010. Clockwise from the right, A8, A5, A6

Alkalinity Titrations were preformed in the field or within a 24 hour period following sample collection at the sedimentology/paleontology lab at the University of Canterbury. Titrations were preformed on 25 ml of filtered water, in a 50 ml beaker (rinsed three times with filtered water), and used 0.01N sulfuric acid and a calibrated pH probe. Alkalinity was calculated using the USGS's web based alkalinity calculator, http://or.water.usgs.gov/alk/, using the gran function plot method.

Sampling following the February 22nd earthquake was performed by Travis Horton (Table 4.2). Samples were filtered on site using a 0.45µm filter and put into a 50 ml test tube, rinsed three times with filtered water, for stable isotope an anionic analysis. These samples were then analyzed at the University of Canterbury.

Site	Sample total
Avon	46
Heathcote	2
Waimakariri	1
Lakes	9
Springs/Pipes	36

Table 4.2 Earthquake Samples

4.4 Sample analysis

The stable hydrogen and oxygen isotope composition of all samples reported in this thesis was determined using a Picarro, Inc. cavity ring-down wavelength spectroscopy liquid water isotope analyzer (model #L2120-i). δD and δ18O values were normalised to the VSMOW scale using a 2-point (i.e. 'stretch and shift') correction based on replicate analyses of the International Atomic Energy Agency's SMOW2 and SLAP certified isotopic reference waters. Accuracy and external precision of the normalized data were determined from replicate analysis of multiple quality assurance standards, including: GISP, TEL1, TEL2, TEL3, TEL4, and an internal laboratory deionized water standard. For all water analyses, 1µl of 0.45µm filtered water was injected into the analyser's vaporizer module using a CTC-combipal autosampler fitted with a gas-tight 10µl SGE syringe. Each sample was analysed 6 times and the first 2 analyses were discarded due to the isotopic memory effect. Certified reference waters and quality assurance standards were analyzed 20 times each at the start and end of each analytical sequence. The first 10 reference/standard analyses were discarded due to the larger memory effect associated with the extreme difference in isotopic composition from one reference/standard to the next. All data are accurate to <±1.0‰ for δD and

<±0.2‰ δ18O.

The stable carbon isotope composition of dissolved inorganic carbon (DIC) was determined using the Spotl (2005) method. In brief, using a disposable plastic syringe fitted with a 20 gauge needle, 1ml of 0.45µm filtered water was injected into an ultra-high purity helium (>99.9999% helium) flushed exetainer vial (10ml borosilicate glass) containing 100µl of >90% phosphoric acid and sealed by a butyl rubber septum-lined plastic cap. Carbon dioxide liberated by the acid-sample reaction was then analyzed for δ13C (and δ18O) using a ThermoFinnigan GasBench II connected to a ThermoFisher Delta V Plus gas isotope ratio mass spectrometer under continuous-flow conditions. External precision and accuracy were established by analyzing certified reference calcite standards, NBS18 and NBS19, at start, middle, and end of each analytical sequence. All reported DIC-δ13C values are precise to <±0.2‰. Internal precision, for all isotopic analyses (δD, δ18O, δ13C) was established by reference gas zero-enrichment (i.e. standard on-off) tests performed immediately prior to each analytical sequence and is <±0.05‰ for all sample runs. Stable isotopic analyses were carried out in the University of Canterbury, Geological Sciences, Stable Isotope Laboratory.

Anion concentrations were determined using a reagent-free ion chromatograph (DIONEX RF-IC 2100) in the Department of Geological Science, University of Canterbury. All samples were 0.45µm filtered prior to analysis. The precision and accuracy of concentration data was established by analyzing six mixed anionic reference standards of known concentrations spanning the 0.001 mg/l to 100 mg/l concentration range.

Chapter 5: Results

5.1 Introduction

This chapter presents the results of the data collected during the course of this thesis. The chapter is divided into three sections, Introduction, Stable Isotope Data and Anion Data. Analysis and discussion of the results appears in the next chapter.

5.2 Stable Isotope Results

5.2.1 Oxygen-18

$\delta^{18}O$ measured during the study period ranged from -9.59 to -1.31‰. Values for samples collected from the Avon River ranged between -9.58 and -4.04‰, while values for the Heathcote River ranged between -8.83 and -1.31‰. Values for the Waimakariri, including a sample taken towards the end of the February 22nd earthquake sampling period, ranged between -9.41 and -8.21‰. The values for the sampling period following the February 22nd earthquake on the Avon River ranged between -9.53 and -2.76. Mean and Median Oxygen-18 values are listed in Table 5.1 and do not show significant differences (T-test;α=0.05). All of these samples fall within the range of observed $\delta^{18}O$ values for meteoric water collected in Christchurch between 2009 and 2011 (Blackstock 2011).

Oxygen 18		
Site	**Mean ‰**	**Median ‰**
Avon River	-8.33	-8.67
Heathcote River	-7.86	-8.37
Waimakariri River	-8.21	-8.82
Earthquake Avon River	-7.92	-8.29
Earthquake Spring	-8.36	-8.27
Earthquake Pipes	-8.45	-8.48
Earthquake Lakes	-7.30	-7.37
Total	**-8.00**	**-8.35**

Table5.1 $\delta^{18}O$ Means and Medians

5.2.2 Deuterium

$\delta^{18}D$ measured during the study period ranged from -74.18 to -9.17‰. Values for samples collected from the Avon River ranged between -74.18 and -26.23‰, while values for the Heathcote River ranged between –59.67 and -9.17‰. Values for the Waimakariri, including a sample taken towards the end of the February 22nd earthquake sampling period, ranged between -69.32 and -54.89‰. The values for the sampling period following the February 22nd earthquake on the Avon River ranged between -9.53 and -2.76. Mean and Median deuterium values are listed in Table 5.2 and do not show significant differences (T-test;α=0.05). All of these samples fall within the range of observed $\delta^{18}D$ values for meteoric water collected in Christchurch between 2009 and 2011 (Blackstock 2011).

Deuterium		
Site	**Mean ‰.**	**Median ‰.**
Avon River	-57.89	-59.42
Heathcote River	-54.01	-57.80
Waimakariri River	-61.34	-54.89
Earthquake Avon River	-54.05	-57.55
Earthquake Spring	-59.08	-58.33
Earthquake Pipes	-56.43	-55.98
Earthquake Lakes	-51.60	-53.28
Total	**-54.87**	**-58.18**

Table 5.2 δD Means and Medians

5.2.3 Carbon-13

$\delta^{13}C$ measured during the study period ranged from -21.04 to -7.12‰. Values for samples collected from the Avon River ranged between -19.37 and -13.83‰, while values for the Heathcote River ranged between –21.04 and -16.98 Mean and Median $\delta^{13}C$ values are listed in Table 5.3 and do not show significant differences (T-test;α=0.05).

Carbon-13		
Site	**Mean ‰.**	**Median ‰.**
Avon River	-16.71	-16.66
Heathcote River	-16.98	-18.36
Total	**-16.64**	**-16.98**

Table 5.3 $\delta^{13}C$ Means and Medians

5.3 Anion Data

5.3.1 Fluoride

Fluoride measured during the study period ranged from .003 to .220 mg/l. Values for samples collected from the Avon River ranged between .014 and .220 mg/l, while values for the Heathcote River ranged between .026 and .120 mg/l. Values for the Waimakariri, including a sample taken towards the end of the February 22nd earthquake sampling period, ranged between .0257 and 0.0363 mg/l. The values for the sampling period following the February 22nd earthquake on the Avon River ranged between 0.003 and 0.110 mg/l. Mean and Median fluoride values are listed in Table 5.4 and do not show significant differences (T-test;α=0.05).

Fluoride		
Site	**Mean mg/l**	**Median mg/l**
Avon River	0.052	0.030
Heathcote River	0.046	0.037
Waimakariri River	0.032	0.035
Earthquake Avon River	0.028	0.025
Total	**0.037**	**0.028**

Table 5.4 Fluoride Means and Medians

5.3.2 Chloride

Chloride measured during the study period ranged from 0.727 to 3167.213 mg/l. Values for samples collected from the Avon River ranged between 3.808 and 3167.213 mg/l, while values for the Heathcote River ranged between 9.579 and 254.205 mg/l. Values for the Waimakariri, including a sample taken towards the end of the February 22nd , 2011 earthquake sampling period, ranged between 0.727 to 3.779 mg/l. The values for the post February 22nd, 2011 earthquake period from the Avon River ranged between 0.727 and 7.662 mg/l. Mean and Median chloride values are listed in Table 5.5 and, despite the large range in values, do not show significant differences (T-test;α=0.05).

Chloride		
Site	**Mean mg/l**	**Median mg/l**
Avon River	254.205	6.457
Heathcote River	62.932	14.305
Waimakariri River	1.868	1.097
Earthquake Avon River	5.445	5.756
Total	**0.037**	**0.028**

Table 5.5 Chloride Means and Medians

5.3.3 Nitrate

Nitrate measured during the study period ranged from 0.450 to 38.778 mg/l. Values for samples collected from the Avon River ranged between 1.108 and 38.778 mg/l, while values for the Heathcote River ranged between 1.815 and 9.474 mg/l. Values for the Waimakariri, including a sample taken towards the end of the February 22nd earthquake sampling period, ranged between 0.450 and 0.629 mg/l. The values for the post February 22nd, 2011 earthquake period from the Avon River ranged between 0.629 and 11.239 mg/l. Mean and Median nitrate values are listed in Table 5.6 and, despite the large range in values, do not show significant differences (T-test;α=0.05).

Nitrate		
Site	**Mean mg/l**	**Median mg/l**
Avon River	6.280	4.813
Heathcote River	9.474	4.919
Waimakariri River	0.533	0.519
Earthquake Avon River	5.577	5.601
Total	**5.642**	**4.893**

Table 5.6Nitrate Means and Medians

5.3.4 Sulfate

Suflfate measured during the study period ranged from 0.314 to 108.444 mg/l. Values for samples collected from the Avon River ranged between 0.900 and 101.827 mg/l, while values for the Heathcote River ranged between 3.471 and 108.444 mg/l. Values for the Waimakariri, including a sample taken towards the end of the February 22nd earthquake sampling period, ranged between 2.868 and 4.392 mg/l. The values for the post February 22nd, 2011 earthquake period from the Avon River ranged between 0.314 and 14.650 mg/l. Mean and Median sulfate values are listed in Table 5.7 and, despite the large range in values, do not show significant differences (T-test;α=0.05).

Sulfate		
Site	**Mean mg/l**	**Median mg/l**
Avon River	11.908	8.226
Heathcote River	24.427	13.239
Waimakariri River	3.880	4.380
Earthquake Avon River	5.233	5.016
Total	**10.091**	**6.702**

Table 5.7 Sulfate Means and Medians

5.3.5 Bromide

Bromide measured during the study period ranged from 0.008 to 34.591 mg/l. Only a handful of Avon and Heathcote samples registered for bromide, while the Waimakariri samples did not have detectible amounts of bromide. Values for samples collected from the Avon River ranged between 0.1907 to 34.591 mg/l, while samples for the Heathcote River ranged between 0.122 and 2.894 mg/l. The values for the post February 22nd, 2011 earthquake period from the Avon River ranged between 0.008 and 0.078 mg/l. Mean and Median bromide values are listed in Table 5.8 and do not show significant differences (T-test;α=0.05).

Bromide		
Site	**Mean mg/l**	**Median mg/l**
Avon River	9.702	2.791
Heathcote River	1.0656	0.181
Earthquake Avon River	0.0384	0.0391
Total	**1.425**	**0.050**

Table 5.8 Bromide Means and Medians

5.3.6 Nitrite

Nitrite measured during the study period ranged from 0.011 to 1.990 mg/l. Only a handful of Avon and a single Heathcote sample registered for Nitrite, while the Waimakariri samples did not have detectible amounts of bromide. Values for samples collected from the Avon River ranged between 0.066 to 1.990 mg/l, while samples for the Heathcote River ranged between 0.464 and 0.464 mg/l. The values for the post February 22nd, 2011 earthquake period from the Avon River ranged between 0.011 and 0.066 mg/l. Mean and Median Nitrite values are listed in Table 5.8 and do not show significant differences (T-test;α=0.05).

Nitrite		
Site	**Mean mg/l**	**Median mg/l**
Avon River	0.660	0.291
Heathcote River	0.464	0.464
Earthquake Avon River	0.039	0.039
Total	**1.425**	**0.050**

Table 5.8 Bromide Means and Medians

Chapter 6: Discussion

6.1 Introduction

The main goals of this thesis were to determine the origins and geochemical composition of the Avon and Heathcote Rivers; to determine the geochemical composition, origin, and impact of surface surface-waters released following of the February 22nd Christchurch Earthquake; and to assess the effectiveness of surface-water geochemical tracers in relation to the Christchurch Groundwater System (CGS). This chapter achieves these goals through the discussion of the geochemical data presented in Chapter 5. First, an analysis of the temporal and spatial trends from the Avon-Heathcote Rivers is presented. Second, the hydrogeochemical impacts of the February 22nd Christchurch Earthquake in comparison to the Avon-Heathcote Rivers are presented. Third, the sources of water for the Avon-Heathcote Rivers are constrained using mass-balance methods. Fourth, the strengths and weaknesses of various geochemical tracers on the Avon-Heathcote Rivers in relation to surface-water groundwater interactions in the CGS are presented.

6.2 Tidal Influences on the Avon and Heathcote Rivers: Variations with Distance and Time

6.2.1 Introduction

The most salient geochemical pattern in the Avon-Heathcote River sites is a pronounced spatial trend I ascribe to tidal influences in the systems. The trend, simply put, is that as the rivers neared the Avon-Heathcote Estuary a shift in stable isotopic compositions towards more positive values, and an increase in the dissolved load concurrently is apparent. Temporal variation is also evident in some sites, however, this patter was not statistically significant (t-test;α:0.5). As the samples collected following the February 22nd Christchurch Earthquake do not cover the same downstream (i.e. eastern) localities which exhibit a spatial trend, they are not included in this subsection and instead will be discussed in section 6.3.

6.2.2 Distance and Temporal Variability

When plotted against distance an increasing trend in the stable isotopic compositions an increase in anion concentrations as the rivers moved toward the Estuary is clearly present (Figures 6.1 & 6.2). This trend was observed during each sampling period, though the trend was considerably muted during the October 2011 sampling period, which was collected during a storm event. The positive trend and enriched anion concentrations were observed at the samples sites A8, A7, H7, and H6, all of which were within 5km of the Avon-Heathcote Estuary. The major anions strongly showing this trend were chloride, fluoride and sulfate (Figure 6.2). In the case of chloride the sites situated within 5km of the estuary were

10 to 100 times more enriched than the average concentrations upstream. Dissolved inorganic carbon (DIC) exhibited this trend only on the Avon River. DIC concentrations for the Heathcote River rose sharply, after the headwater sampling site, to values associated with the downstream reaches of the Avon River, and stayed relatively constant, ±10 mg/l, along the course of the river.

The stable isotopes $\delta^{18}O$, δD and $\delta^{13}C$, all exhibited a positive trend as samples moved towards the estuary. In the case of $\delta^{18}O$ and δD a rise in values occurred only in the sites closest to the estuary, A8 and H7. The stable isotope $\delta^{13}C$ exhibited a sharp rise of 2‰ following site A3 and proceeded to remained relatively constant along the river until reaching site A8, where it rose another 2‰. The Heathcote River by contrast exhibited a gradual rise in $\delta^{13}C$ along its course; however, this may simply be the result of a lack of $\delta^{13}C$ samples near the headwaters. The $\delta^{13}C$ values for the Heathcote River are comparatively negative to the Avon River, and indicative that the Heathcote River is experiencing more biological (i.e. microbial) activity along its course.

The only anion constituent for which this trend was not observed was nitrate. The amount of nitrate remained relatively constant across the length of the river and within 5km of the Estuary tended to remain constant or decrease in concentration. There was one exception to this with the February 2012 sample from A8 had an unusually large concentration of nitrate. Bromide and Nitrite only occurred in a few of the samples during the June 2011 – February 2012 sampling period, and with a single exception for bromide, were not detected at sites outside of 5km from the Estuary.

The sites within 5km of the Estuary also exhibit the greatest temporal variability in the June 2011 – February 2012 sampling period. Average standard deviation for sites A8, A7 & H6 was 220.52, 48.30, & 2.49, respectively. Temporal variability, on the Avon sites at least, is considerably higher than the average standard deviation of upstream sites, which were 2.27. Heathcote estuary sites overall appear to have lower temporal variability compared to the Avon River. The Heathcote may exhibit more variability, as the site H7 was excluded from this comparison, as it was only sampled twice and lacked anion data for a sampling, meaning a measure of overall temporal variability could not be established.

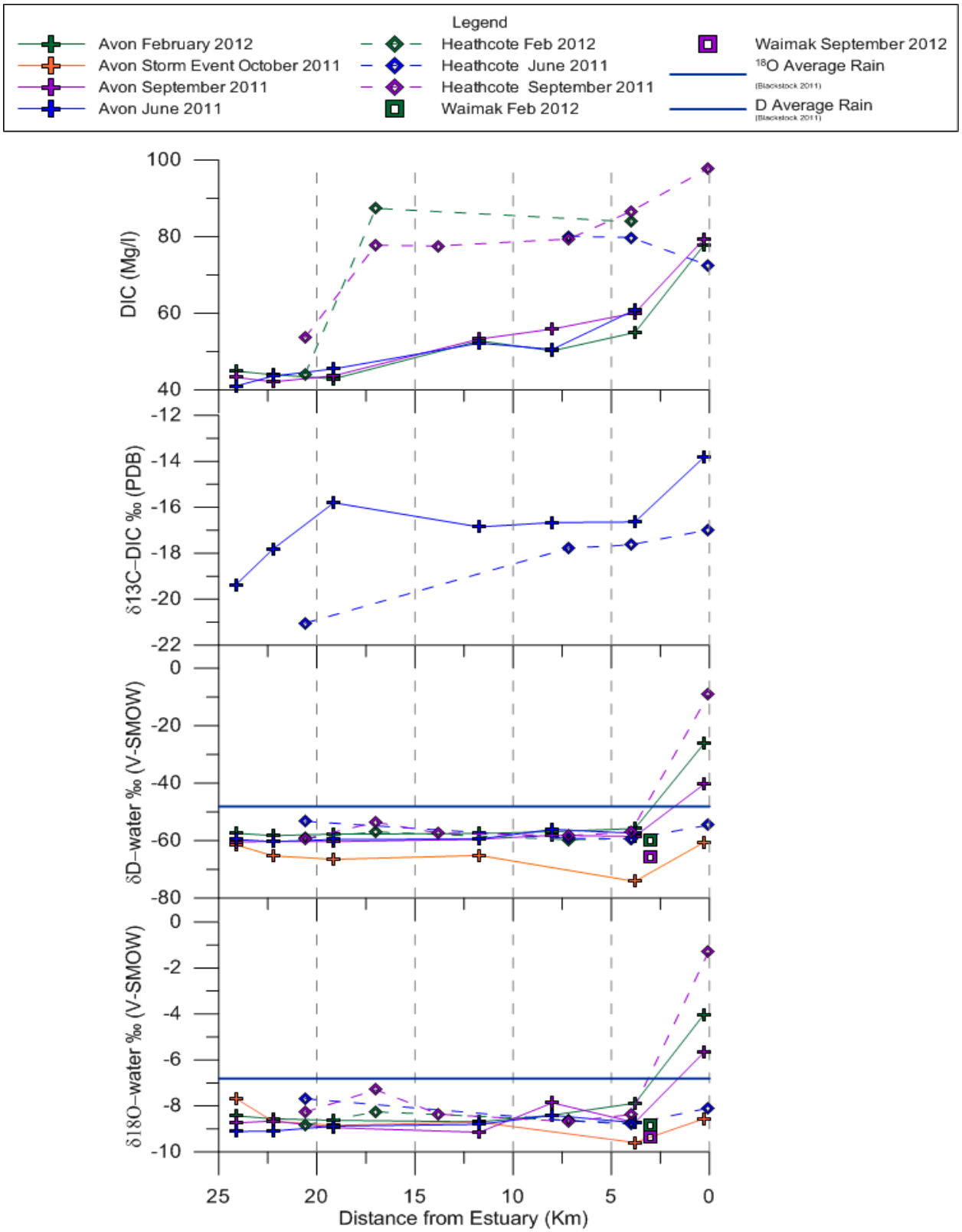

Figure 6.1 Variations with distance and time: stable isotopes $\delta^{19}O$, δD, $\delta^{13}C$ and dissolved inorganic carbon

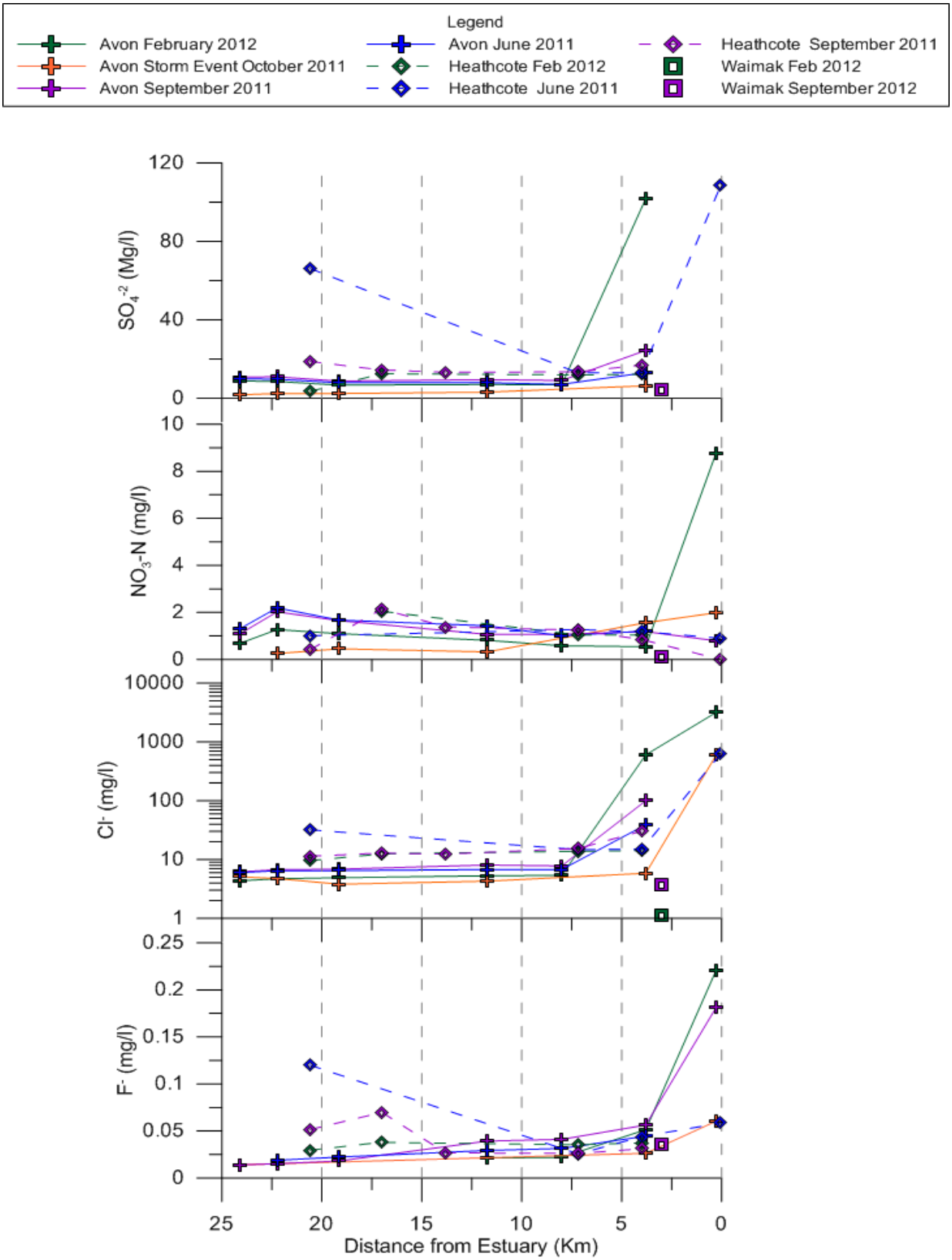

Figure 6.2 Variations with distance and time: fluoride, chloride, nitrate-N, and sulfate

The site H2, the sampling site furthest upstream on Heathcote River, is the only major outlier for the observed spatial and temporal trends. This site's chloride and sulfate values, with averages of 17.66 and 29.49 mg/l respectively, were high in comparison to other upstream sites, which had average Chloride and sulfate values of 9.00 and 9.28 mg/l respectively. The site H2 also exhibited stable isotopic values, which were positive compared to the average values of sites upstream. H2 also exhibited the highest overall temporal variability outside of the tidal zone; however, compared to the average temporal variability for upstream sites this was not statistically significant (t-test; P-value=0.87). The fact H2 is an outlier can be explained by the physical conditions of the site. Flow at this site was generally low to almost stagnant depending on sampling period. These conditions could have allowed the surface waters to evaporate, concentrating anions, as well as creating relatively positive stable isotope signatures, and would explain the greater variability between sampling periods as weather conditions could easily affect evaporation rates.

6.2.3 Interpretation of the spatial and temporal variability: Tidal Influences

If the anionic data presented above were interpreted individually this data would suggest that mixing of waters was occurring near the estuary from potentially multiple sources, e.g. water sourced from urban discharge or contaminated by leechate. When taken in conjunction with the stable isotope data however, the simpler interpretation for this trend would be the mixing of brackish or salt with the river waters near the estuary due to tidal effects. The stable isotope values for $\delta^{18}O$ and δD at sites A8 and H7 are comparable to those of oceanic waters. The high chloride values of >100mg/l, present in sites within 5 km of the Estuary, indicate mixing of salt waters with freshwaters. The fact nitrate does not conform to the spatial trend, as concentrations stay the same or decrease slightly towards the Estuary, is consistent with this theory. As average oceanic concentrations of nitrate are very low (~.62 mg/l) (Hem 1985), no change or even a slight dilution of nitrate concentrations would be expected. Attempts to estimate the amount of oceanic water present near the estuary using average oceanic geochemical composition (Hem1985) gave inconsistent results between datasets; for example, from the site A8 in the June 2011 sampling period, a model using chloride indicates 10% oceanic water while the sulfate model indicates that .07% the water is oceanic. Sampling was also conducted so that both high and low tides were represented in different sampling periods, indicating that oceanic mixing is present during all tidal phases. Tidal influences would also explain the large temporal variation exhibited in sites within 5km of the Estuary, as these sites would respond more rapidly to outgoing or incoming tides.

Tidal effects were noted on the Avon and Heathcote Rivers prior to the Christchurch Earthquake Sequence in relation to flow, but there is no aqueous geochemical data in the mainstream literature for comparison to sites within the tidal zone. There are reports (Beavan et al 2011, Beavan and Motagh 2012) that the eastern suburbs in the areas around the Avon River have been downthrown 50 mm following the Christchurch Earthquake Sequence due to liquefaction, lateral spreading and compaction. These reports (Beavan et al 2011, Beavan and Motagh 2012) also indicate the area surrounding the Heathcote River in contrast to this has been upthrown, experiencing uplift of 20-40mm. Post-earthquake subsidence on the Avon River may have increased the extent of observable tidal effects on the river, while post-earthquake uplift on the Heathcote River may have reduced the extent of observable tidal effects. Without pre-earthquake geochemical data for comparison, this is merely speculative and could be an avenue of further research.

6.2.4 Summary: A geochemical comparison of the Avon and Heathcote Rivers

When comparing all the geochemical indicators between the Avon and Heathcote Rivers, with the exception of DIC, there is no statistical difference in the geochemistry of the waters (t-test;α:0.5). The higher DIC concentration of DIC in the Heathcote River is statistically significant (t-test; p-value:0.001) compared to the Avon River and could be explained by differences in catchment lithology. The catchment of the Avon River is predominately glacial fluvial outwash comprised of inert greywacke, whereas the catchment for the Heathcote includes parts of Banks Peninsula, and extinct volcanic complex. Silicate weathering of volcanic rocks from Banks Peninsula could explain the higher DIC concentrations in the Heathcote. A tidal zone is present on both rivers with tidal influences occurring to approximately 5km upstream of the Avon-Heathcote Estuary. Comparing spatial and temporal geochemical trends on both rivers suggests that the Avon River has a slightly larger tidal influence compared to the Heathcote River.

6.3 Effects of the February 22nd earthquake on geochemistry

6.3.1 Introduction

The waters collected following the February 22nd, 2011 Christchurch Earthquake provide a unique opportunity to assess the effects of a large near-field earthquake on surface hydrology in an urban environment. This section compares the post-earthquake samples to samples from the June 2011 – February 2012 (post-earthquake) quarterly period. At the coarsest scale, the post-earthquakes samples were geochemically similar to quarterly values from the Avon and Heathcote Rivers; however, some

important outliers present in the data can shed light on post-earthquake surface-water, urban-water, and groundwater interactions. Post-earthquake river samples were all collected outside of the tidal zone, as established above, and are compared to only to the quarterly samples from the same geographic sampling area.

6.3.2 Observations: Similarities, differences and variability

Overall the surface waters sampled following the February 22nd, 2011 Christchurch Earthquake were geochemically similar, in stable isotopic composition and anionic concentrations, to quarterly samples taken from the Avon and Heathcote Rivers from the period of June 2011 to February 2012. As the post-earthquake samples were not analyzed for $\delta^{13}C$, nor for alkalinity, comparison of these tracers cannot be carried out. Comparing the stable isotope values for $\delta^{18}O$ and δD between the earthquake and quarterly sampling periods, there was no statistically significant difference between the sampling sets and values fell within similar ranges (t-test; α=0.05, $\delta^{18}O$ p-value: 0.34, δD p-value:0.24)(Figure 6.3**)**. The post-earthquakes sites exhibited average $\delta^{18}O$ and δD values of -7.99‰ and -55.45‰, ±1‰, respectively. These samples were also within the observed range of meteoric values for the region (Blackstock 2011) as well as the range of meteoric samples collected during the course of the thesis.

The major anion concentrations exhibited both similarities and differences between the post-earthquake and quarterly samples. Anion analysis was only done for river samples, the overwhelming majority of which were taken from the Avon River, with a single sampling day representing the Waimakariri. With the exception of bromide, post-earthquake anion values exhibited a similar range to the quarterly samples. The anion constituents chloride, nitrate, and nitrite showed no statistical difference (t-test;α=0.05) between post-earthquake and quarterly samples. It is worth noting, however, that nitrite is only present only in the post-earthquake samples and not found at detectable concentration in the quarterly samples. The anions bromide, fluoride and sulfate showed statistically different signatures between the post-earthquake and quarterly periods (Figures 6.4 and 6.5). The post-earthquake anion data also show a similar spatial trend to the quarterly samples, with anion concentrations increasing slightly with distance downstream.

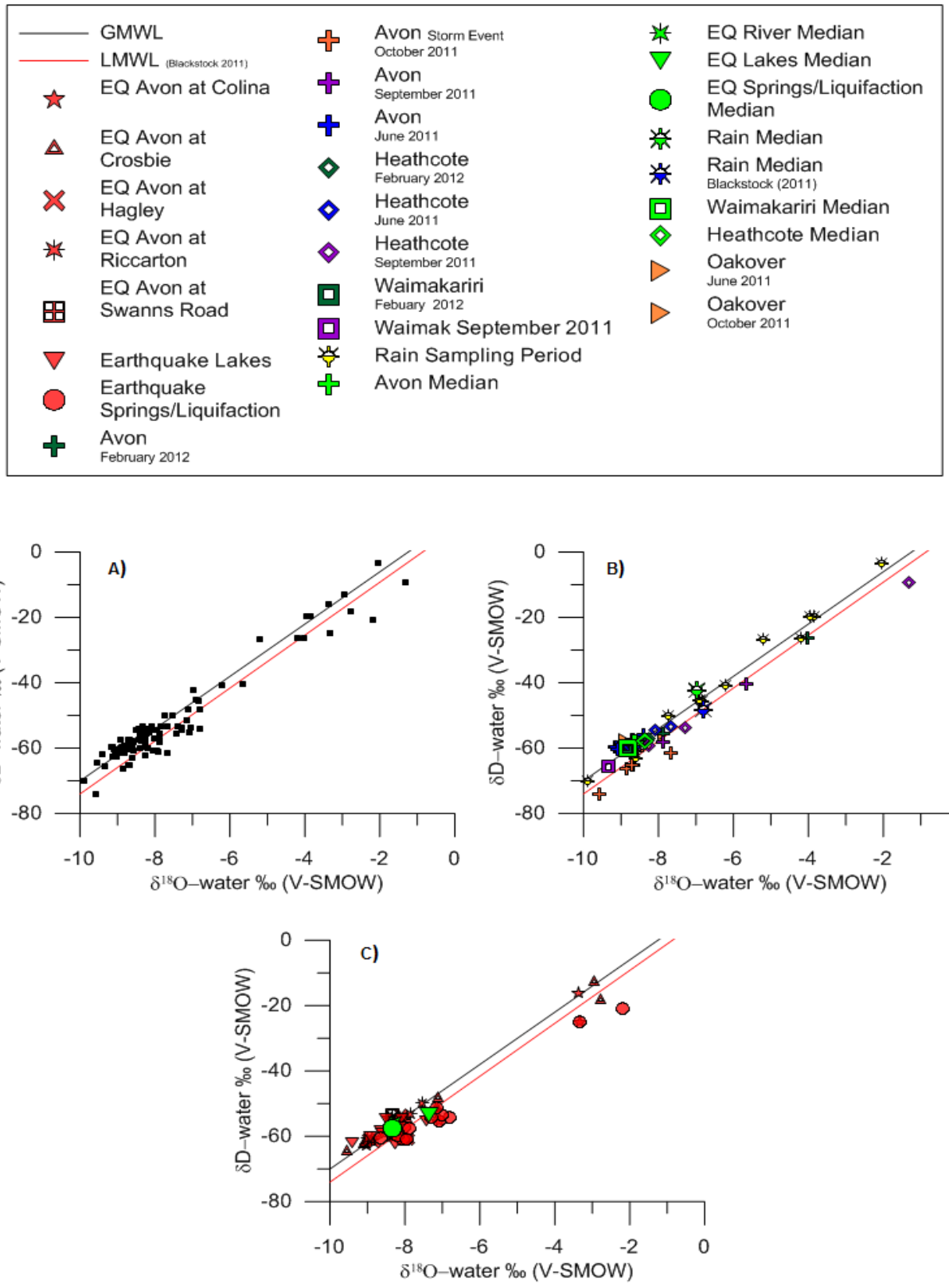

Figure 6.3 Stable isotopes $\delta^{18}O$ and δD: A) all samples collected in this thesis B) July 2011-February 2012 sampling period C) Post February 22nd, 2011 Earthquake sampling period

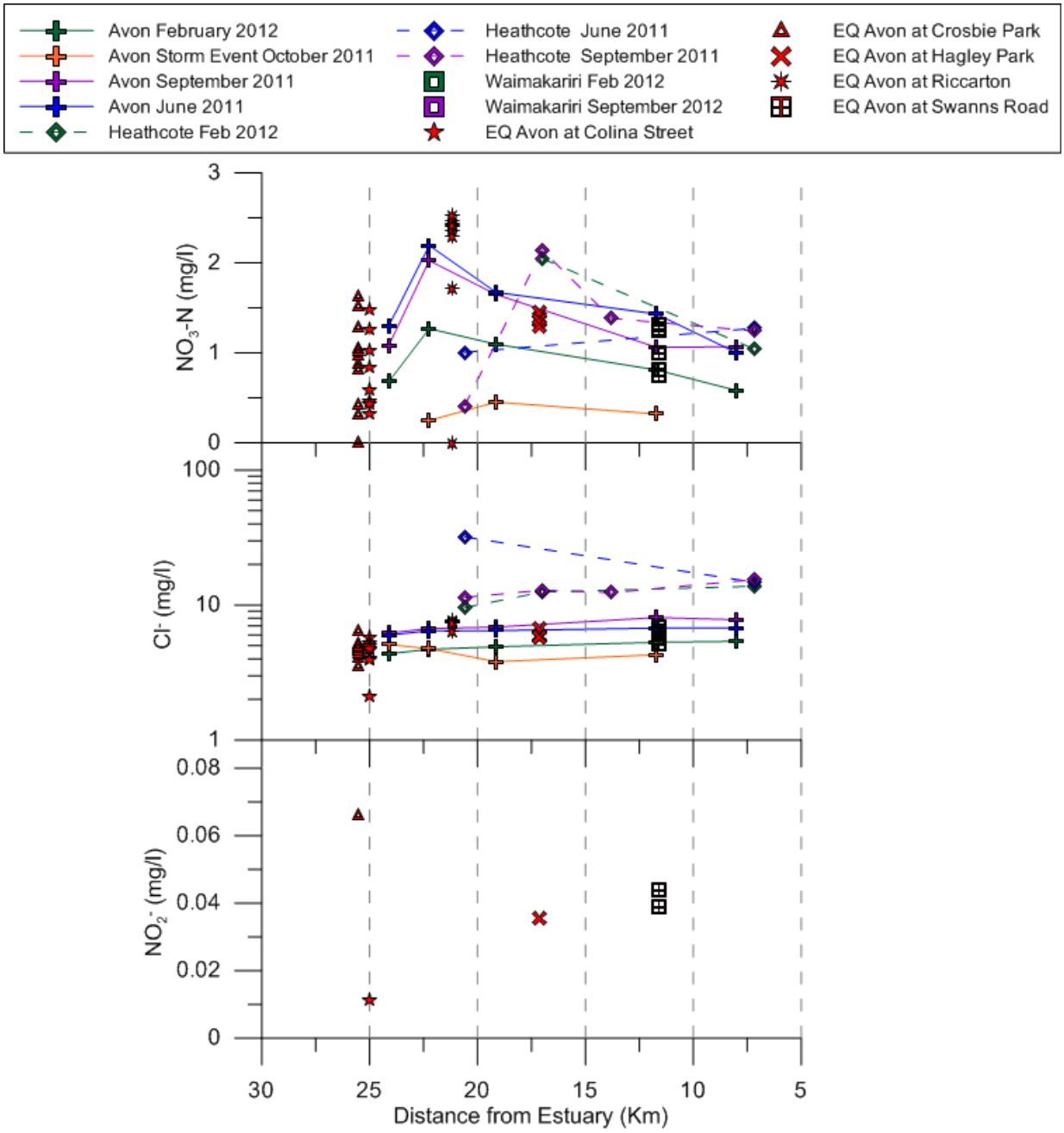

Figure 6.4 Anion constituents which show no significant difference between post-earthquake and quarterly Avon-Heathcote River samples

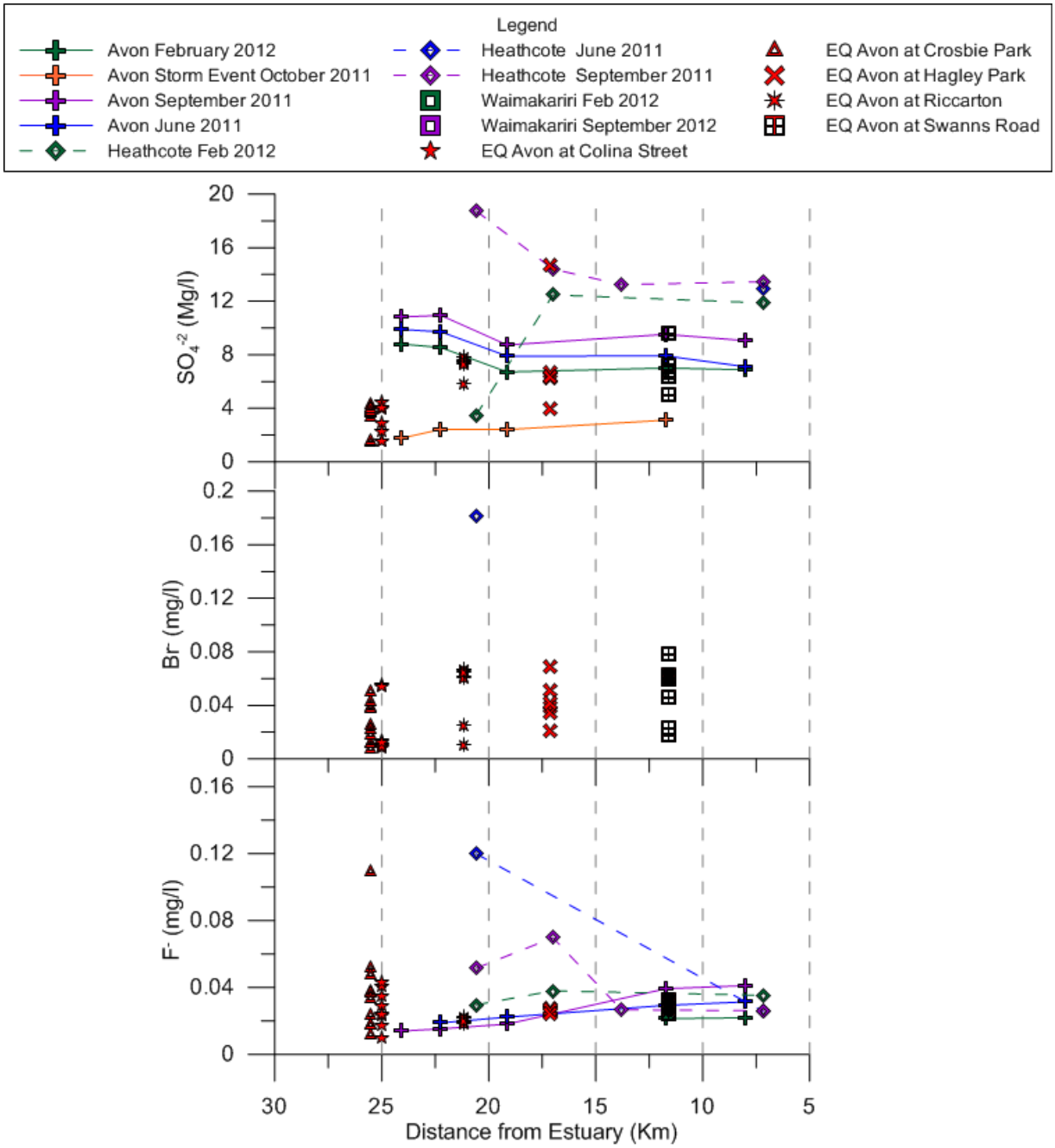

Figure 6.5 Anions which show significant difference between post-earthquake and quarterly Avon-Heathcote Rivers samples

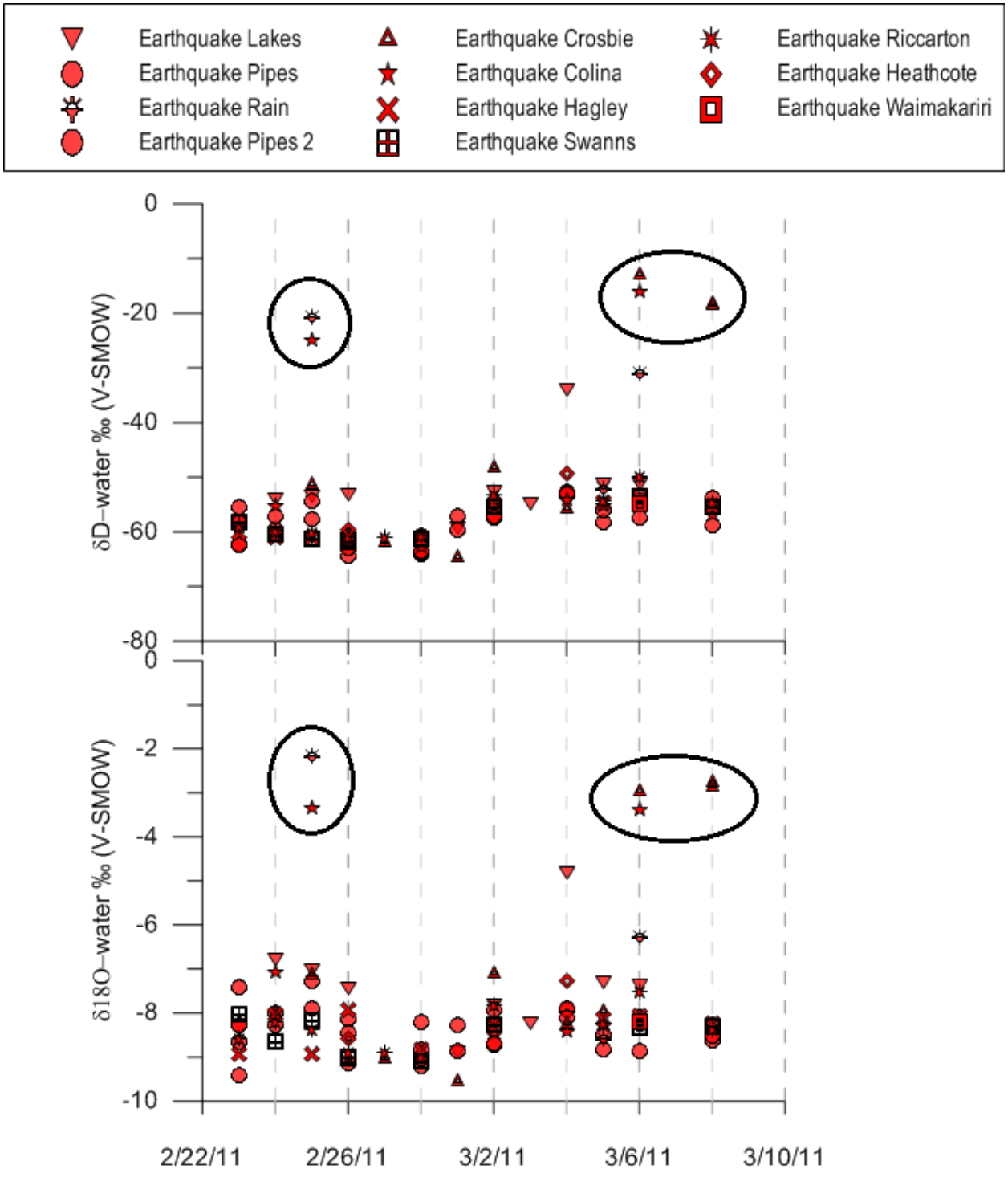

Figure 6.6 Variations in stable isotopes δD and $\delta^{18}O$ by distance and date following the February 22nd, 2011 Christchurch Earthquake. The outliers at Crosbie Park and Colina Street are circled in black. The single isotopically positive lake sample is the result of evaporation of surface waters following the earthquake

When examining the overall temporal variability for the geochemical datasets between the post-earthquake and quarterly sampling periods, there was no statistical difference between the two periods (t-test; α=0.05). When examining temporal variability between individual sampling locations, two post-earthquake sites, the Avon at Crosbie Park and the Avon at Colina Street, exhibited statistically significant temporal variability (t-test; α=0.05, p=.0002) (Figure 6.6). These sights exhibited the highest variability of the post-earthquake samples with standard deviations of 3.38 and 3.64 respectively.

6.3.3 Surface Water – Groundwater interactions follow the February 22nd earthquake

By comparing the geochemical constituents between the post-February 22nd earthquake samples and the quarterly sampling period on the Avon-Heathcote Rivers, a number of inferences can be made about the surface-water, groundwater, and urban-water interactions following the February 22nd, 2011 Christchurch Earthquake. The majority of surface-waters released following the February 22nd earthquake appear isotopically similar to the waters flowing through the Avon and Heathcote Rivers.

Despite the fact the post-earthquake waters and the Avon-Heathcote Rivers quarterly samples appear to be statistically similar, the outliers from the post-earthquake samples indicate that more complex groundwater, urban-water, surface-water interactions occurred following the February 22nd, 2011 Earthquake. The outlier stable isotopic values from Crosbie Park and Colina Street are as positive as the values associated with oceanic influence in the tidal zones (Figure 6.6). Taken alone, these outliers could be the result of meteoric events enriched in ^{18}O and D, or perhaps the result of urban influences, e.g. a burst pipe carrying waters from emergency reservoirs which had evaporated in storage. The anion data, particularly the statistically different bromide values, provides addition evidence for sources of these outliers and their relationship to the overall impact of the February 22nd Christchurch Earthquake.

Chloride and bromide have been used as conservative tracers in hydrogeochemical studies; in particular Cl^-/Br^- ratio has been used to differentiate different sources of water in groundwater systems (Table 6.1) (Davis et al 1999). The median Cl^-/Br^- ratio for post-earthquake samples was 133.8, implicating shallow groundwater as a major source of water in the Avon River following the February 22nd Christchurch Earthquake. Along with the shallow groundwater signature, there are samples, mostly from Crosbie Park and Colina Street, which have a Cl^-/Br^- ratio indicative of domestic sewage.

Water Source	Cl^-/Br^- Ranges
Atmospheric Precipitation	50 – 150
Shallow Groundwater	100 – 200
Domestic Sewage	300 – 600
Summer Urban Runoff	10 - 100

Table 6.1 Ranges for Cl^-/Br^- ratios in natural waters (Davis et al 1999)

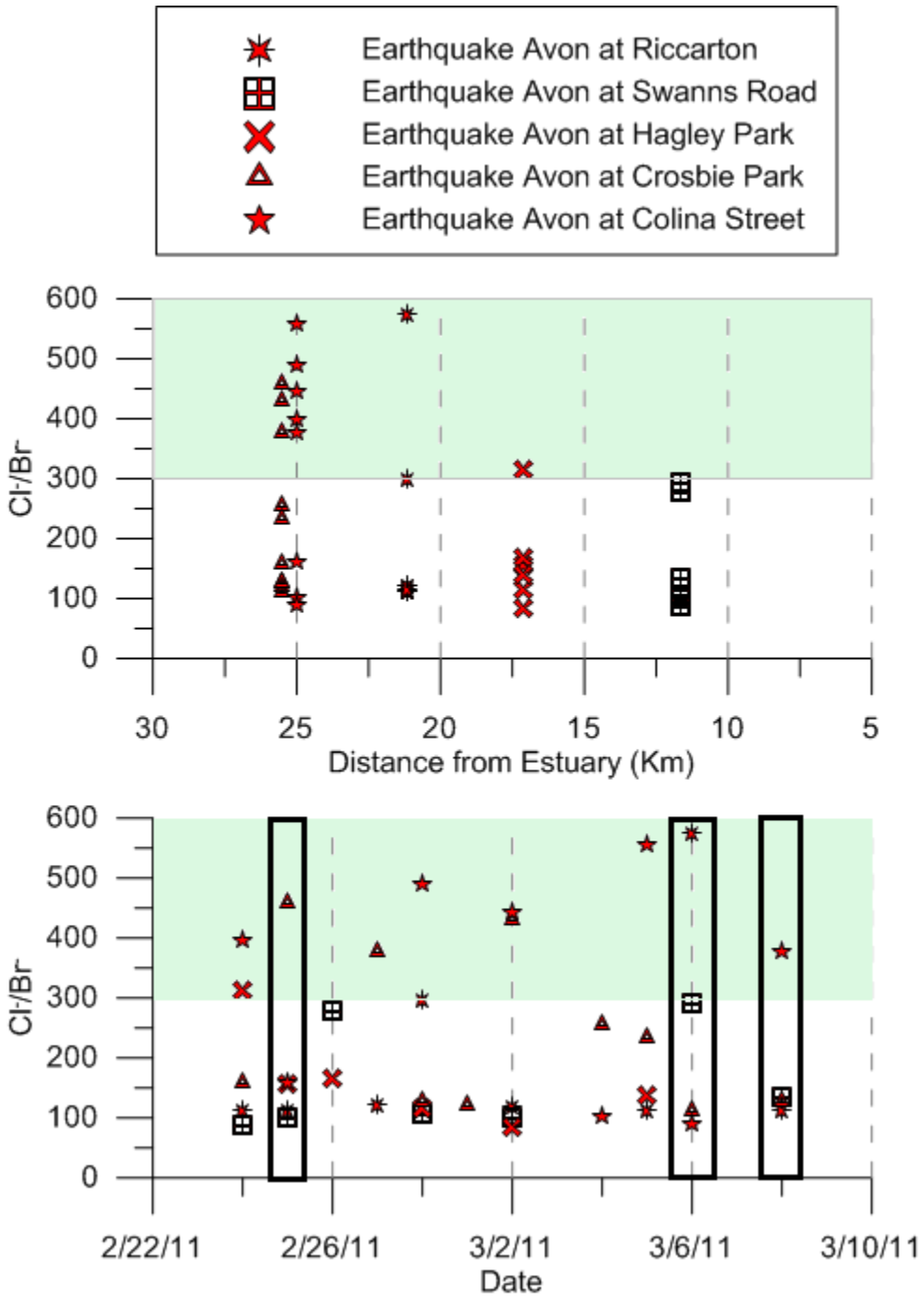

Figure 6.7 Chloride/Bromide Ratios by date and distance: The shaded area is the range of Cl^-/Br values associated with domestic sewage while the black boxes represent dates of observed stable isotope outliers.

The relatively strong signal of sewage discharge at these locations was unexpected as they are both headwater sites in the western suburbs, which experienced far less infrastructure damage than the eastern suburbs. It seemed reasonable from this to expect a stronger sewage signal downstream towards the eastern suburbs. In the course of collecting samples, however, a large sinkhole had formed

from either a broken sewage or water main, directly upstream of Crosbie Park and Colina Street at Whithells Road. As Crosbie Park and Colina Street are essentially at the headwaters for the Avon River, these sites would have comparatively lower flow to sites downstream, and it would therefore be expected that the impact of urban discharge would have been diluted as flow increased downstream due to natural surface discharges.

Urban discharge, particularly the broken water/sewage main near the headwater sites on the Avon River, is almost definitely the source of the sewage signature at these sites. The stable isotope outliers in the geochemical data occur either on or within a day of higher Cl^-/Br^- ratios. They do not occur at the same sites, though Crosbie Park and Colina Street are in close proximity to one another. While it is possible that urban discharge could be the source of the stable isotope outliers, this theory requires further evidence.

6.4 Sources of Avon Heathcote Rivers: Geochemical tracers in the Christchurch Groundwater System

6.4.1 Water Sources for the Avon and Heathcote Rivers

In examining the geochemical data collected in the course of this thesis it is very clear that the water sourcing the Avon and Heathcote Rivers, as well as the surface waters released following the February 22nd earthquake, originate predominately from groundwater. Both the Avon and Heathcote Rivers, with median $\delta^{18}O$, δD values of -8.67‰,-59.42‰ and -8.37‰,-57.80‰ respectively, are isotopically negative compared to the average meteoric waters (Blackstock 2011), with values of -6.81‰,-48.12‰ (Figure 6.8). These values also fall between the global meteoric water line and Blackstock 2011's local meteoric water line (Blackstock 2011) (Figure 6.9). Given the low temporal variation in stable isotope compositions on the Avon and Heathcote Rivers compared to the large variations seen in meteoric waters during the course of the sampling period and as documented by Blackstock 2011, it is highly unlikely that meteoric water is a major contributor to these rivers. The low stable isotope variability on the Avon and Heathcote Rivers indicates that the water is coming from an isotopically stable source, strongly implying groundwater as the major source for both rivers, as groundwater attenuation causes mixing, which in turn dampens the variation between independent rainfall events. This finding is not surprising and supports previous hydrological models for the Avon River (Cameron 1992, White 2009).

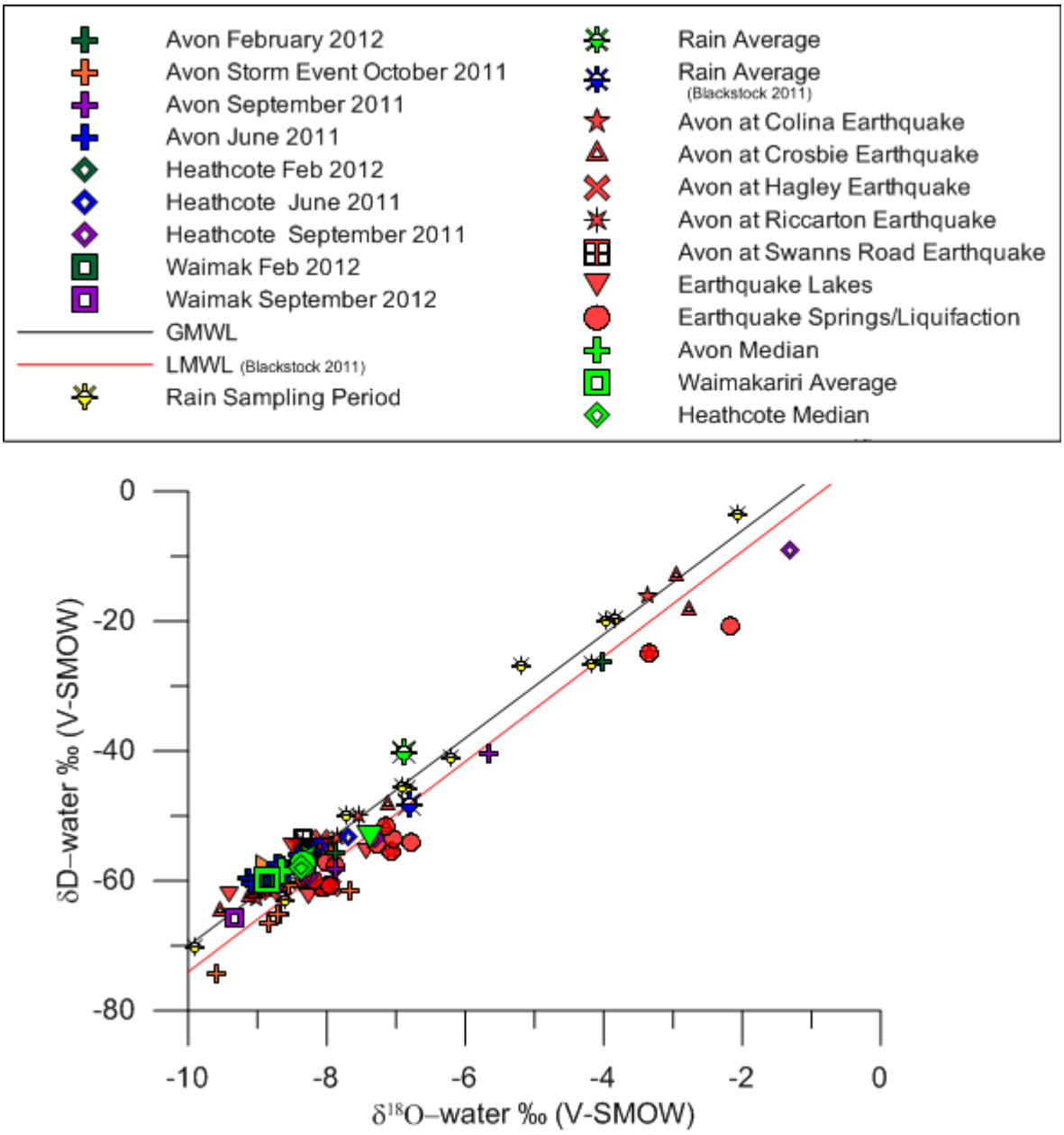

Figure 6.8 $\delta^{18}O$ and δD Bivariate plot: note the Averages for the Avon Heathcote and Waimakariri.

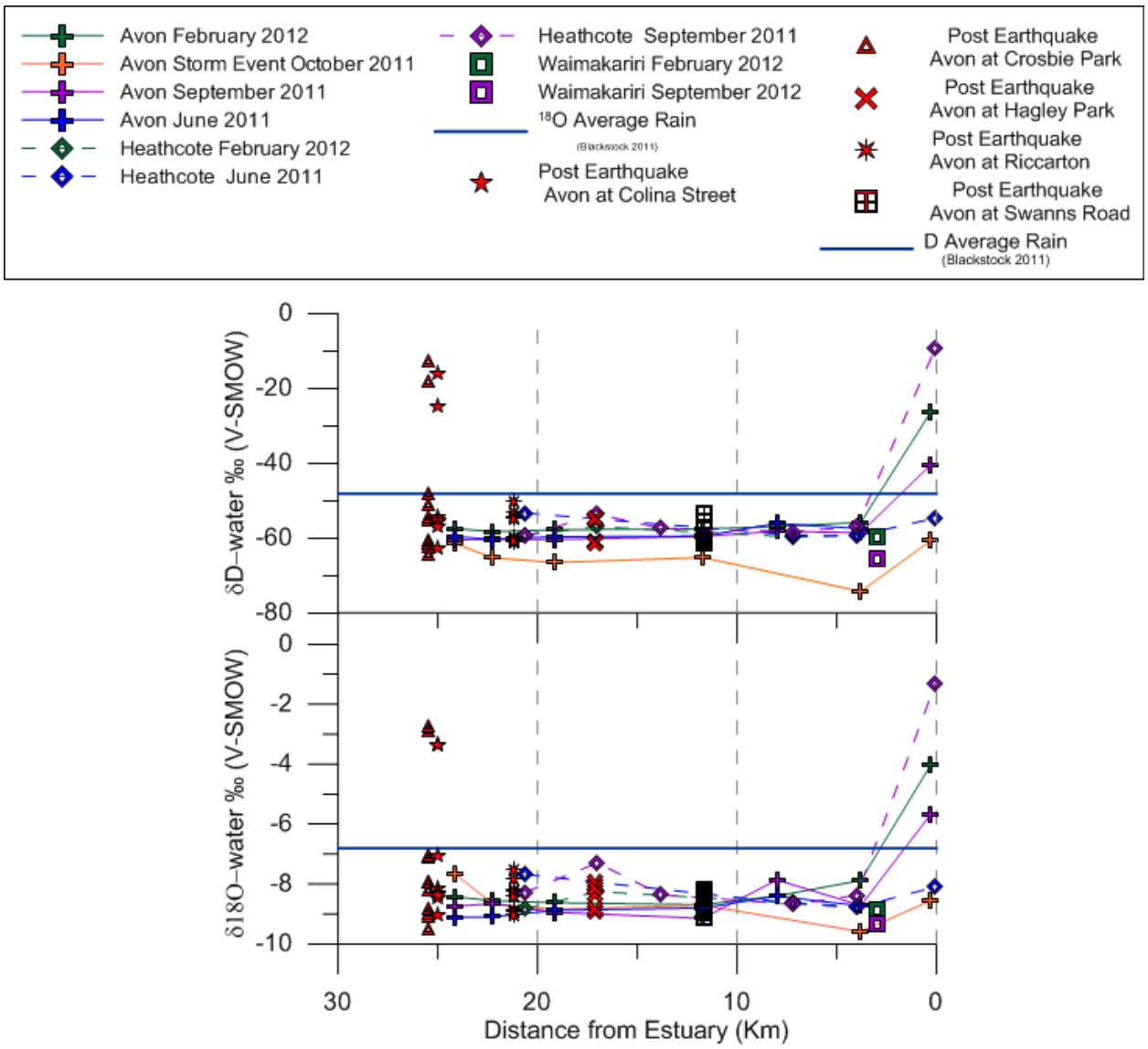

Figure 6.9 Stable Isotope concentrations on the Avon and Heathcote rivers: note that the rivers are consistently below the average rainwater composition for Christchurch (Blackstock 2011)

6.4.2 Tracing the origins of the groundwater sources for the Avon and Heathcote Rivers.

Attempting to define and compare the relative contributions of groundwater sources (i.e. aquifers) for the waters of Avon and Heathcote Rivers is difficult using the present geochemical data available for comparison. In the data collected for the Avon and Heathcote Rivers to that of Waimakariri River during the sampling period, every geochemical tracer was statistically insignificant (t-test;α:0.5). White's (2009) model suggests that groundwater, coming from the Waimakariri and flowing along former flood channels, contributes to the base flow of the Avon River. Stewart's (2012) geochemical work,

particularly his analyses using $\delta^{18}O$,$\delta^{13}C$ and DIC, indicate that the shallow groundwaters entering the CGS, covering the same region of this White's (2009) model, are derived primarily from Waimakariri 'Alpine' waters with some mixing of groundwater with a meteoric signature, possibly from the Central Canterbury Plains. Stewart (2002), using $\delta^{18}O$, based on an average Waimakariri value of -9.5‰, made a model to identify the relative origins of groundwaters in the CGS as coming from alpine (i.e. Waimakariri) water, inland rainfall recharge groundwater from the Central Canterbury Plains, or a mixture of both. Based on this model, the groundwater from Avon River is approximately 60% 'rainwater recharge groundwater', while groundwater from the Heathcote River is approximately 75% 'rainwater recharge groundwater' (Figure 6.10) (Stewart et al. 2002).

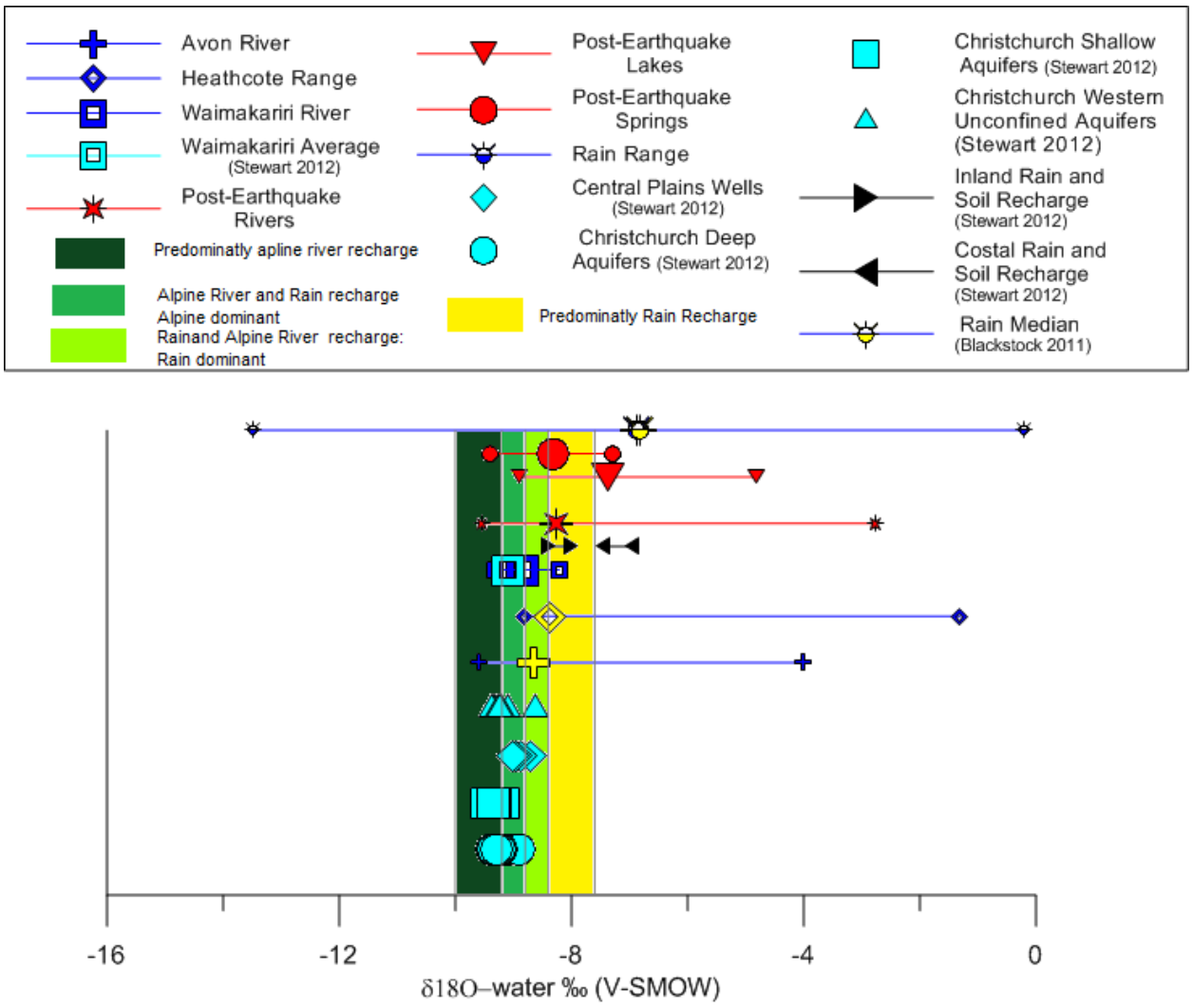

Figure 6.10: $\delta^{18}O$ median values and ranges for the sampling period combined with Stewart 2002's scale for recharge sources in the Christchurch–West Melton Groundwater Sector. Modified from Stewart 2012.

Compared to other models based on different geochemical tracers, these models conflict with the $\delta^{18}O$ model, which indicates that 60%-75% of water in the Avon and Heathcote Rivers is being sourced by inland meteoric groundwater. Stewart (2012) included another model to indicate rainfall amounts and groundwater sources in the CGS, which functioned by plotting $\delta^{13}C$ against 1/DIC. This model works by triangulating samples between the $\delta^{13}C$ /(1/DIC) values of biogenic carbon, the average values for the Waimakariri, and an estimated value for rainfall recharged groundwater, which is assumed to have low DIC but acquires a $\delta^{13}C$ signature from interaction with biogenic carbon. When using this model, the amount of rain recharged groundwater on the Avon River sites ranges from 54% to 10%, with an average influence of 24.4% that is significantly lower than value of approximate 60% from the $\delta^{18}O$ model (Figure 6.11). This model cannot be applied to the Heathcote River, or to two of the Avon River sites, as they plot outside zone necessary to triangulate approximate recharge amounts. This could be due to a number of factors. The Avon sites, for instance, are from the tidal zone and likely have $\delta^{13}C$ values related to marine carbonate due to mixing with oceanic waters. The Heathcote sites, however, are from outside the tidal zone; it is possible that this is due to the influence of carbon sources from silicate weathering within the Heathcote River's catchment. Another possibility, which I believe to be the case, is that there is more variability in the $\delta^{13}C$ and DIC values for the Waimakariri than is currently acknowledged. When comparing the $\delta^{13}C$ /(1/DIC) to the $\delta^{18}O$ model, it must be noted that $\delta^{13}C$ values for the Avon and Heathcote Rivers were only collected for the June 2011 sampling period and $\delta^{13}C$ values may have significantly more variability.

Stewart (2012) argues that the estimates using δ13C /(1/DIC) model are correct, because when plotting $\delta^{18}O$, Chloride, Sulfate, and Nitrate-N against the δ13C /(1/DIC) recharge estimate, a linear relationship is exhibited along the mixing line between Waimakariri and 'inland' rainfall recharged groundwaters. When examining the Avon River estimates in this manner, there is no clear relationship exhibited (Figure 6.12). This non-relationship could be attributed to the limited number of samples for which the δ13C /(1/DIC) model could be applied, or it is possible that anion values, for the Avon-Heathcote Rivers have a coastal rather than inland meteoric signature. Stewart (2012) mentions that an analysis for coastal rainfall values has been carried out, but no data for it has been published.

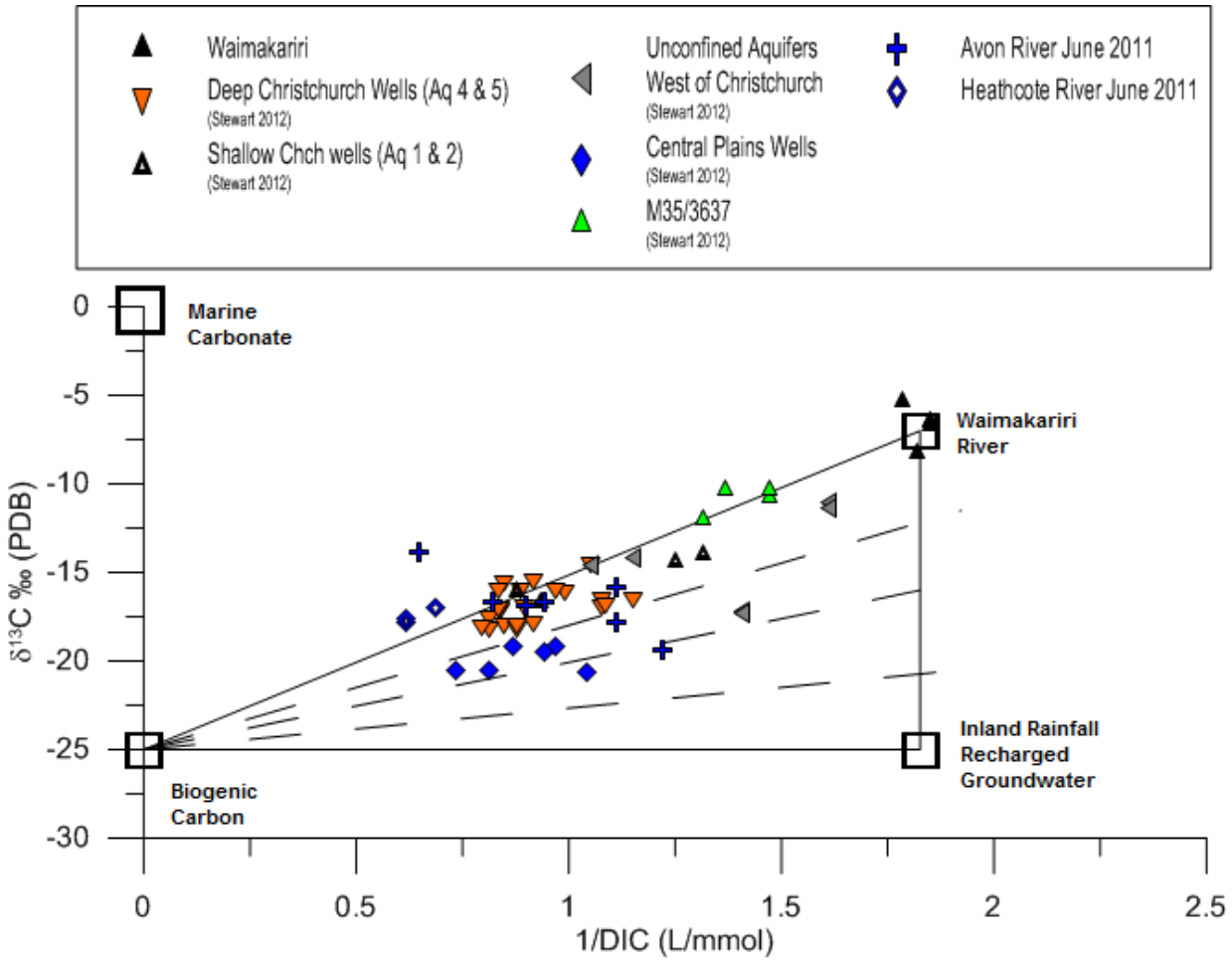

Figure 6.11 Using δ13C/1/DIC to Estimate Groundwater using the Stewart (2012) model

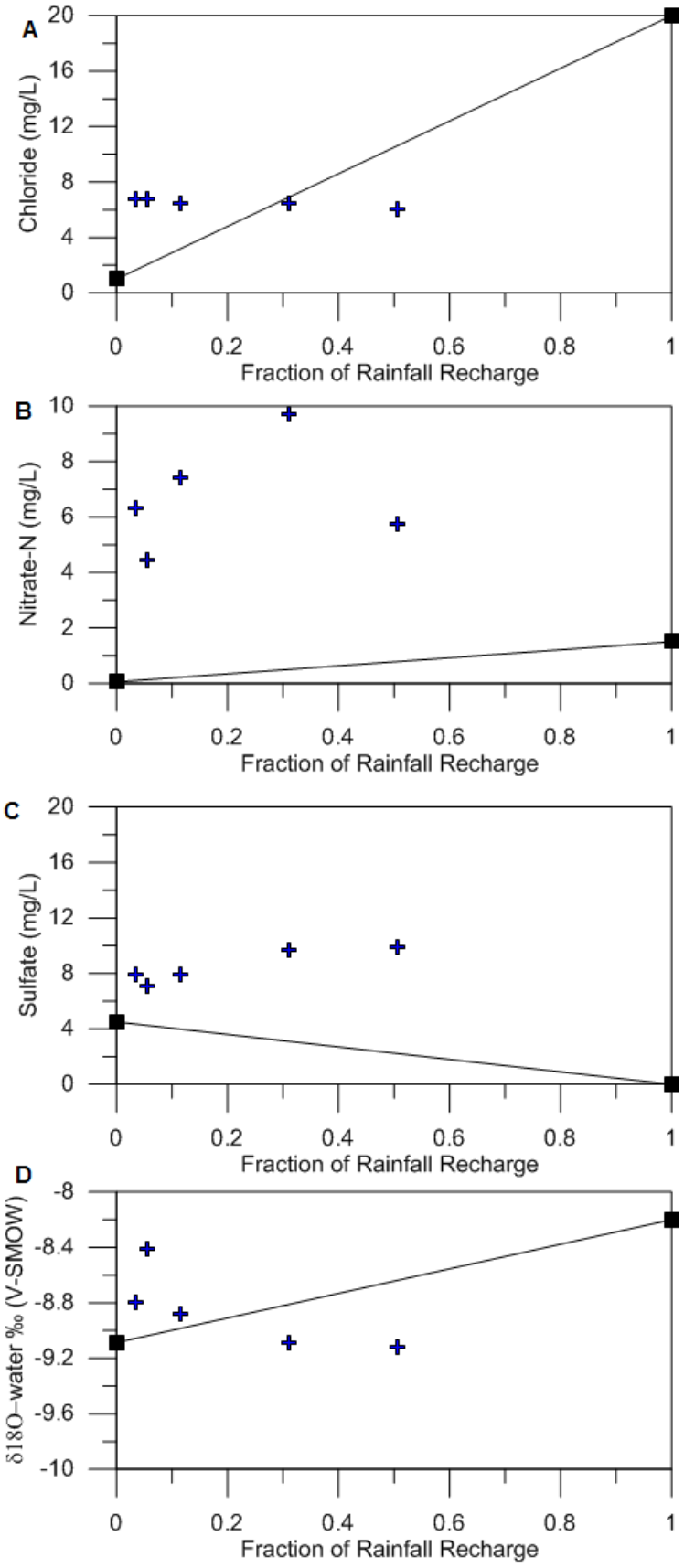

Figure 6.12 (a-d) Rainfall Recharge fractions versus A) Chloride B) Nitrate-N C) Sulfate, D) $\delta^{18}O$

Another comparison of the Avon and Heathcote Rivers to the CGS can be made using a bivariate plot of $\delta^{13}C$ against $\delta^{18}O$ (Figure 6.13). Based on this plot the Avon and Heathcote Rivers appear to be similar to water samples from the deep Christchurch aquifers. This could possibly indicate that deeper waters flowing upward under artesian pressure are entering the system. It could also be an effect of biological factors within the river. Without more samples from the Avon, Heathcote, and especially Waimakariri to account for variability, this observation, while interesting, cannot be considered strong.

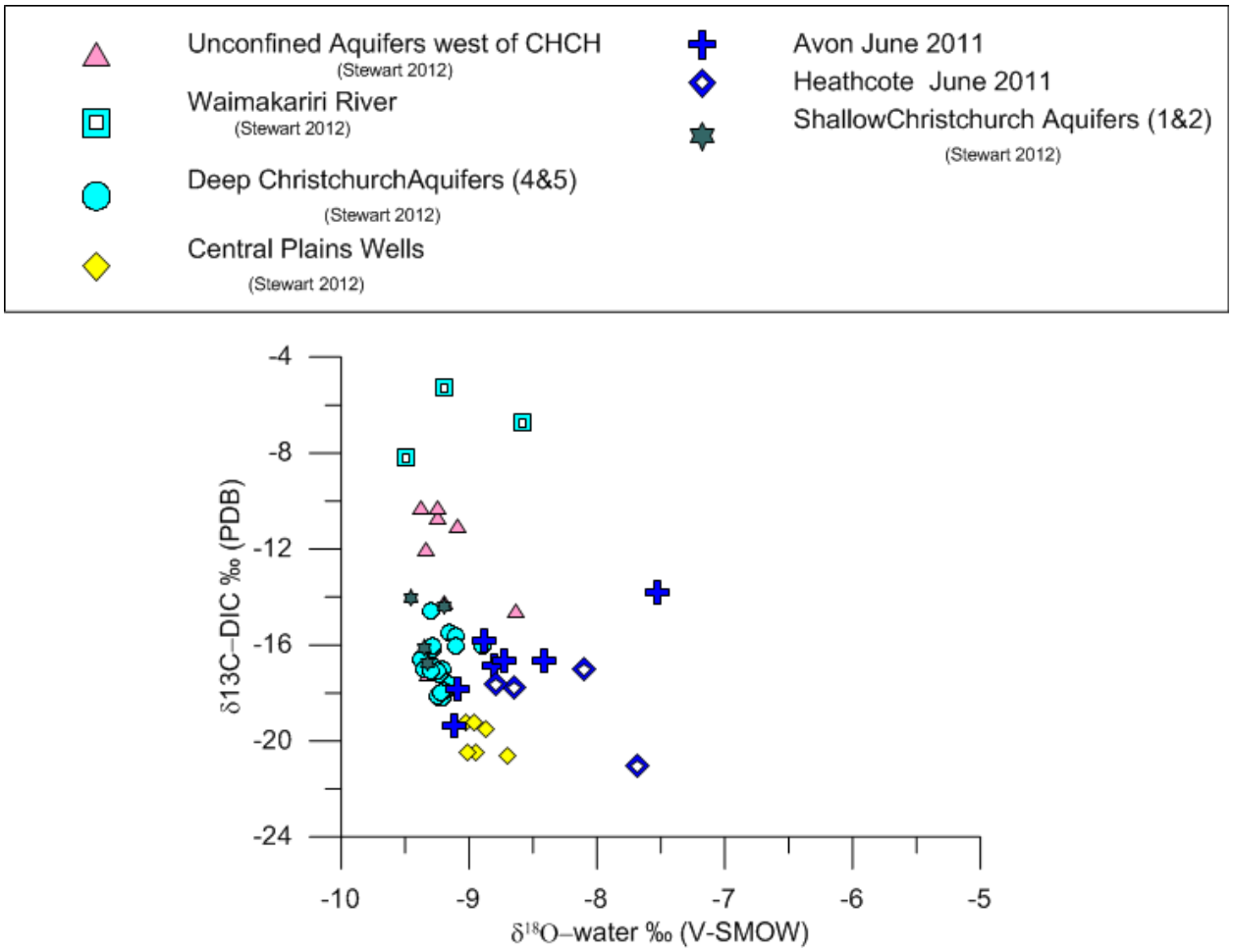

Figure 6.13 $\delta^{13}C$ X $\delta^{18}O$ bivariate plot including data from (Stewart 2012)

6.5 Effectiveness of Geochemical Tracers in the Christchurch Groundwater System

6.5.1 Introduction

As stated in the previous subsection, identifying and quantifying sources of the groundwater feeding the Avon and Heathcote Rivers is challenging, with different geochemical tracers giving different results for the proportion of alpine recharged versus rainfall recharged groundwaters. This subsection aims to explain how effective the current geochemical tracers are and how geochemistry can be better applied in these systems. Stewart 2012 makes an ideal comparison for effectiveness of tracers as his work analyzes 40 years of work with isotopes and geochemistry on the CGS and incorporates most of the major studies for the system including but not limited to, Hanson and Abraham 2009, Stewart 2002, Hayward 2002, Brown and Weeber 2001, Taylor 1989, Taylor and Fox and NCCB 1986. Two main issues with geochemical studies on the CGS became apparent in this study. The first issue is that a broader suite of geochemical tracers should be applied to these systems. The second issue is that there appears to be larger variability in the system, particularly on the Waimakariri, that needs to be addressed.

6.5.2 Effectiveness of Geochemical Tracers

The vast majority of geochemical work on the CGS has involved using ^{3}H and ^{14}C for dating waters and using the stable isotope $\delta^{18}O$ and major ions as tracers. There has been $\delta^{13}C$ analysis done on these systems as well; however, the numbers of samples run for this analysis is small compared to the other tracers. The stable isotope δD has been run on some samples from the CGS, but is not presented in published data and was only used to confirm the expected liner relationships with the global meteoric water line. Furthermore, there is no indication in the literature as to whether δD has been collected since 1989 (Taylor 1989, Taylor 1996). The lack of deuterium data and analysis is very unfortunate because while δD and $\delta^{18}O$ both provide useful information on their own, they cannot be used alone to distinguish individual sources (Figure 6.14). When using these stable isotopes in conjunction, they can provide far higher resolution between sources (Figure 6.15). To highlight the difference in resolution between using only $\delta^{18}O$ and using a δD-$\delta^{18}O$ δD-$\delta^{18}O$ bivariate plot, two examples from this thesis are presented. Comparing only $\delta^{18}O$ values for average meteoric composition between this thesis and Blackstock 2011, the two periods are almost identical (Figure 6.14). When comparing these two values using a δD-$\delta^{18}O$ bivariate plot, however, it is clear the meteoric values from this thesis and Blackstock are substantially different from one another (Figure 6.15). In another example, the October Avon River samples, taken during a southerly storm, and the average Waimakariri River appear to be very similar when only $\delta^{18}O$ is taken into account. A δD-$\delta^{18}O$ bivariate plot clearly shows these two samples are

different. In both of these cases, using only $\delta^{18}O$ as a tracer would incorrectly lead to a conclusion that the waters are geochemically similar and probably from the same source.

While the δ18O-δD bivariate plots, provide better resolution between relative sources, the overall the averages between the Avon, Waimakariri, and Heathcote Rivers still cannot be clearly distinguished from one another, with most samples plotting in a similar range (Figure 6.15). Without δD values for the CGS, this data cannot be compared to the regional context, and the evaluations made for the CGS based solely on δ18O values should be taken in light of this fact.

For this thesis, the stable isotope, $\delta^{13}C$, in conjunction with DIC values, actually appeared to be the most promising way to compare samples and attempt to quantify groundwater sources. Due to the limited number of samples analyzed for this isotope, the observations based using these tracers are not conclusive. As collecting and processing samples for $\delta^{13}C$ has become much easier in recent years (Spotl 2005), more research should focus on this isotope to better understand its variability and controls within the CGS.

On their own the major ions couldn't distinguish various groundwater sources between sites sampled during this thesis (Figure 6.16). As previously stated, no trends were noticed when attempting to plot estimated 'rainfall recharged groundwater' against major ions in the system. The use of Chloride to bromide ratios was extremely useful in determining water origins following the February 22nd earthquake. As bromide was not detected outside the tidal zone during the quarterly sampling, its usefulness in geochemical studies for this system remains limited. Bivariate plots between major anions failed to indicate any substantial trends and are listed in Appendix A. While major ions do not provide high resolution between sources in this system, they still provide useful information when combined with other geochemical indicators.

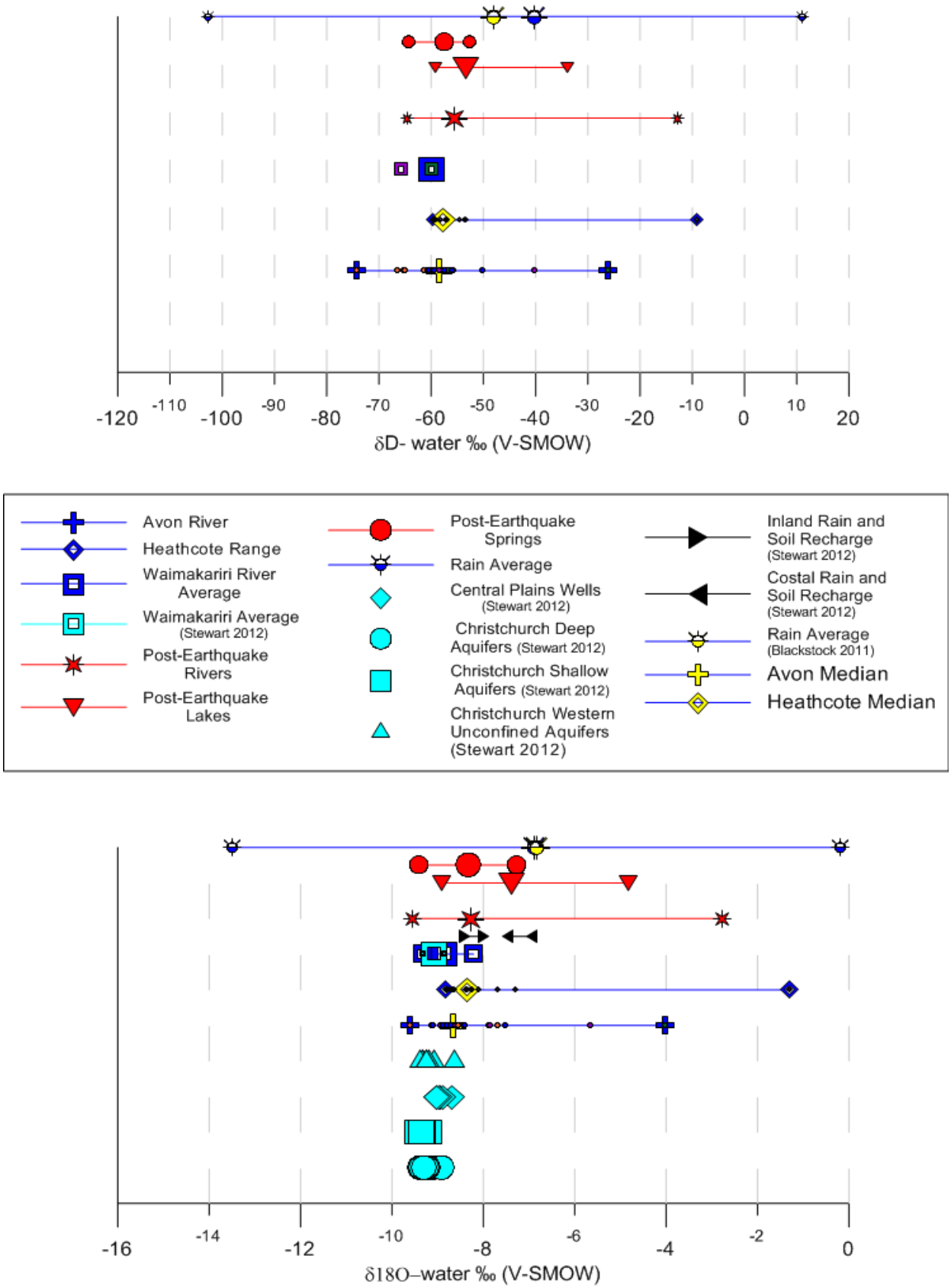

Figure 6.14 Stable Isotopes δD and $\delta^{18}O$ average values, individual values and ranges

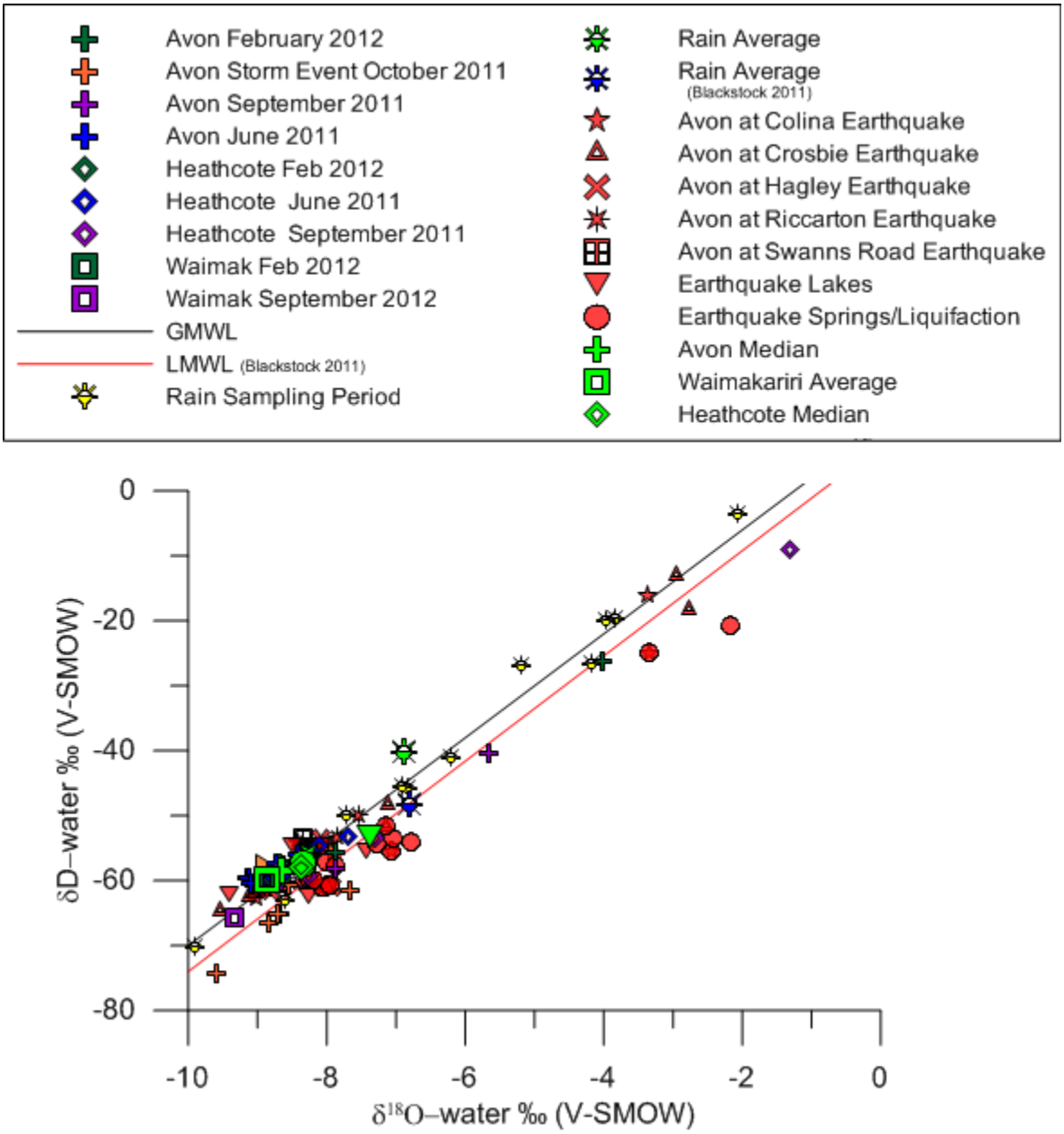

Figure 6.15 $\delta^{18}O$ and δD Bivariate plot: note the average values for the Avon Heathcote and Waimakariri.

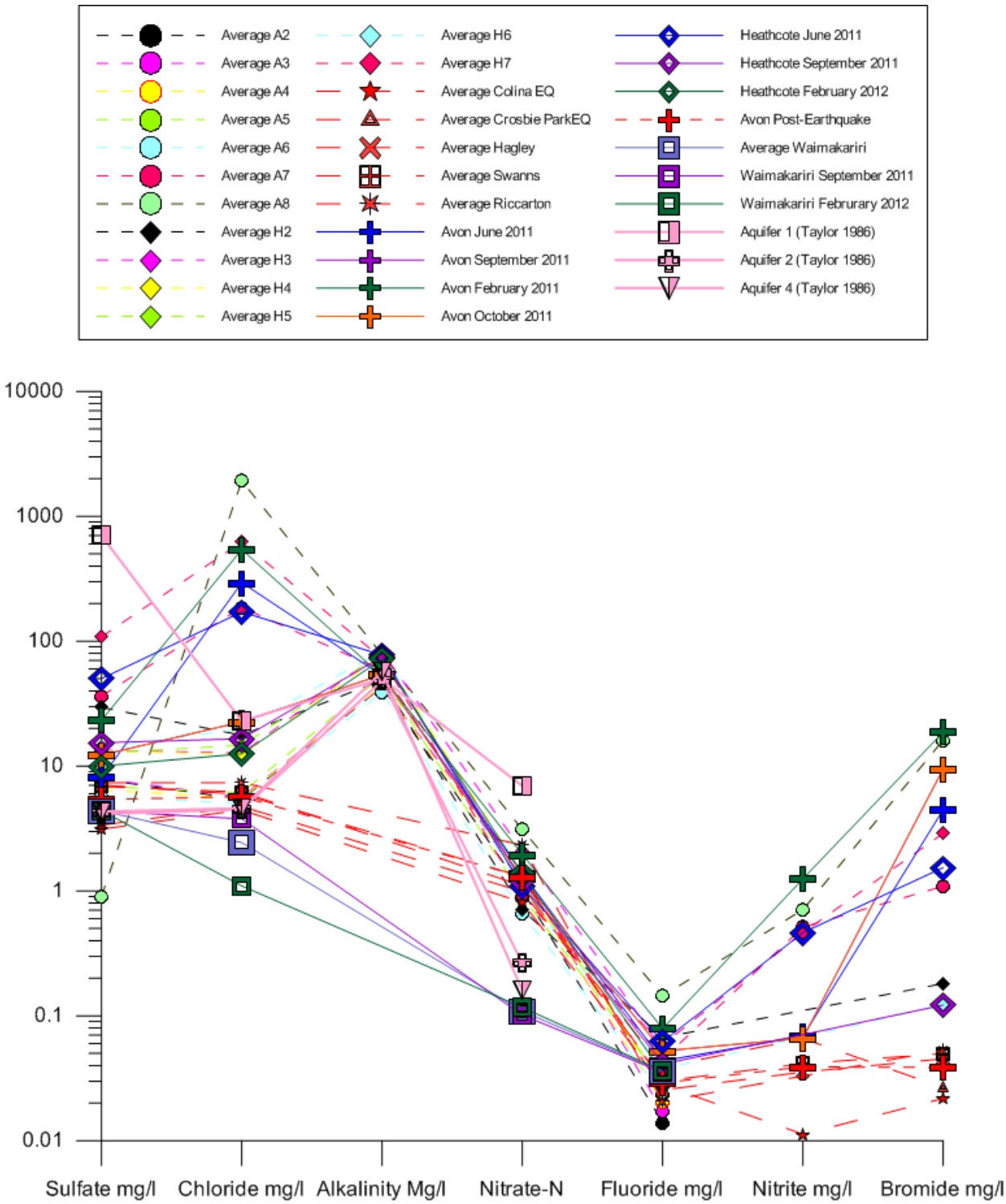

Figure 6.16 Major Anions for the CGS

6.5.3 Variability in the CGS and implications for the Canterbury Plains

There has been over 40 years of study on the CGS and the Central Canterbury Plains, but with available geochemical data, the relationship of groundwaters in the CGS to Avon-Heathcote Rivers still remains ambiguous. One reason for this ambiguity is a lack of acknowledgement and poor understanding of variability within the system, which is particularly apparent in the case of the Waimakariri River. Understanding variability, especially at the inputs to the system, is critically important to developing accurate mixing models.

There is a huge range of values, from -13.49‰ to -0.20‰ for $\delta^{18}O$ and -102.61‰ to 10.97‰ for δD, for stable isotope compositions of Christchurch meteoric waters collected during this thesis. An earlier thesis by Blackstock (2011), also noted similar ranges and large variability in meteoric precipitation for the CGS. The Avon and Heathcote Rivers also exhibit a considerable range in isotopic composition (Figure 6.13). Most importantly it appears that the Waimakariri is far more variable than acknowledged in the literature. As the Waimakariri is an end member for geochemical models related to the CGS, variability could significantly affect results of mixing models. To demonstrate the impact of variability, I applied the Stewart (2002) model to published δ18O values for the Waimakariri from Stewart (2012), which had samples from 1986, 1993, and 2006. The average value for the Waimakariri from this data falls into "Alpine River Recharge and Rain Recharge: Predominately Alpine River". This would incorrectly indicate that the water in the Waimakariri River is 25% to 50% sourced from inland rainwater recharged waters. When Waimakariri samples from this thesis are applied to the Stewart (2002) model the values range from 'predominately alpine river recharge' to 'predominantly rainfall recharged'.

The Waimakariri value or values used to make the Stewart (2002) model are not cited and could be -9.35‰, from a single Waimakariri sample in March 1997, or could come from an average of -9.43‰ collected from a 1977 – 1981 sampling, Stewart et al (1983), which is referenced in Stewart (2012), though I have been unable to locate this published work. Talbot et al (1986) also references a 1979 report by Taylor and Stewart, which I have also been unable locate, which documented Waimakariri River $\delta^{18}O$ ranges from -9.7‰ to -9.2‰ over sampling periods in the 1970s, though these values fall within typical analytical error or ±0.3‰ for $\delta^{18}O$ at that time (Figure 6.10)(Stewart 2002). The fact remains, however, that recent values and averages from the Waimakariri River, reflect that the $\delta^{18}O$ is either more variable or could have changed with climate since the previous studies.

Chapter 7: Conclusions and Future Research Directions

7.1 Conclusions

1. The Avon and Heathcote Rivers both exhibited significant temporal variability, along with positive stable isotopic values and higher anion compositions, within 5km of the Avon-Heathcote Estuary. This was interpreted as resulting from the mixing of rivers waters with salt waters due to the effect of tides.
2. Waters from the Avon and Heathcote Rivers have the same geochemical compositions for the stable isotopes, $\delta^{18}O$ and δD, as well as most anions. Values for DIC and the stable isotope $\delta^{13}C$ were different between the two rivers with the Heathcote River having higher concentrations of DIC and more negative $\delta^{13}C$ values.
3. The surface waters collected following the February 22nd, 2011 earthquake were indistinguishable from quarterly samples taken from the Avon and Heathcote Rivers, when comparing the stable isotopes, $\delta^{18}O$ and δD.
4. The chloride to bromide ratio in the post-earthquake samples from the Avon River has a signature which indicates that most of the water released into the River is sourced from shallow groundwater. However, clear signs indicative of domestic sewage are present in some samples near the headwaters of the Avon River. This is attributed to a burst water main near those sampling sites.
5. Waters for the Avon and Heathcote River system exhibit low variance and isotopically negative $\delta^{18}O$ and δD values when compared to meteoric waters, which indicates the rivers are sourced from groundwaters.
6. Attempts to estimate recharge sources for the Avon-Heathcote groundwaters using published models for the CGS yielded results that were not consistent t between models.
7. No single geochemical tracer provided high resolution between groundwater sources, and interpretations made using only $\delta^{18}O$ can easily be misconstrued.
8. The stable isotopes $\delta^{18}O$ and δD, when used together provide better resolution than using either individually, but do not provide enough resolution to distinguish the Waimakariri River from the Avon or Heathcote Rivers.
9. Use of stable isotope $\delta^{13}C$, in conjunction with $\delta^{18}O$ and DIC, appears to offer higher resolution between groundwater sources in the CGS, but sample sizes for these constituents are limited.

10. There appears to be more variability for the Waimakariri River then is currently recognized in the published literature.

7.2 Further Research Directions

1. Monitoring of surface waters, groundwater and meteoric waters for the stable isotopes, $\delta^{18}O$, δD and $\delta^{13}C$, is needed in for the Christchurch Groundwater System and adjacent Central Canterbury Plains.
2. Long term geochemical monitoring of the Waimakariri River and its catchment area is needed to account for the variability in this system.

Chapter 8: Bibliography

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APPENDIXES

Please see attached PDFs for Appendix A and B

APPENDIX A: ANION BIVARIATE PLOTS

APPENDIX B: SAMPLING DATA